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Distribution of Trihalomethanes in
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THE EFFECT OF BROMIDE ON THE FORMATION AND DISTRIBUTION
OF TRIHALOMETHANES IN CHLORINATED GROUND WATER

by

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FOREWORD

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water systems. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. The Clean Water Act, the Safe Drinking Water Act, and the Toxics Substances Control Act are three of the major congressional laws that provide the framework for restoring and maintaining the integrity of our Nation's water, for preserving and enhancing the water we drink, and for protecting the environment from toxic substances. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Water Engineering Research Laboratory is that component of EPA's Research and Development program concerned with preventing, treating, and managing municipal and industrial wastewater discharges; establishing practices to control and remove contaminants from drinking water and to prevent its deterioration during storage and distribution; and assessing the nature and controllability of releases of toxic substances to the air, water, and land from manufacturing processes and subsequent product uses. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

The objective of this research was to define the effect of bromide, pH, reaction time, and chlorine concentration on the formation and distribution of trihalomethanes in a chlorinated ground water.

Frances T. Mayo, Director
Water Engineering Research Laboratory

ABSTRACT

Trihalomethanes (THM's) are formed during the chlorination of waters as a result of the reaction between chlorine and naturally occurring aquatic organic compounds and humic substances. The effect of bromide ion at various concentrations of chlorine, pH, and reaction time were studied. All of these interact and influence the formation and distribution of individual trihalomethanes (THM's).

Addition of bromide, longer reaction time, higher pH, and higher chlorine concentration were all found to increase the yield of trihalomethanes. The chlorine concentration corresponding to the break point resulted in THM yield less than that observed for the chlorine concentrations on either side of the break point. This phenomenon is as yet unexplained.

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I. INTRODUCTION

It has been established that trihalomethanes (and other halogenated compounds) are formed during water treatment, from the reaction of halogens with organic matter (Stevens et al., 1976; Symons et al., 1981). Two national surveys (Symons et al., 1975; Brass et al., 1977) found that nearly all of the water supplies sampled contained trihalomethanes. In Florida, a survey was conducted which showed that 32 percent of the treated drinking water samples contained above 100 ug/L total THM's while 12 percent were above 300 ug/L total THM's (Beeman et al., 1978).

The U.S. Environmental Protection Agency amended the National Interim Primary Drinking Water Regulations to specify a maximum contaminant level of 0.10 mg/L for total trihalomethanes. The Safe Drinking Water Act (Public Law 93-523) requires that every drinking water regulation contain a statement as to treatment techniques water utilities can employ to achieve compliance with the regulation as well as the maximum contaminant level. It is known that ammonia, bromide, pH, temperature, total organic carbon, and chlorine concentration all interact and influence the formation and distribution of individual trihalomethanes (THM's) during water treatment. There has been no study of the combined effects of the above.

The objective of this research was to define the effect of bromide, pH, reaction time, and chlorine concentration on the formation and distribution of trihalomethanes in a chlorinated ground water.

II. LITERATURE REVIEW

Trihalomethanes are regulated because of their perceived adverse health effects, their ubiquitous occurrence in chlorinated water and because they serve as indicators of other organochlorine compounds in water supplies. By the reason of the potential health hazards associated with the long term ingestion of these halogenated organic compounds, a regulation has been promulgated to limit the total trihalomethane concentration to 100 ug/L in drinking water (Federal Register, 1979).

A nation-wide program has been developed to provide alternatives for reducing trihalomethanes in drinking water. Treatment alternatives have been published which address precursor removal (Kuhn and Sontheimer, 1979; Cotruvo and Sontheimer, 1979) by activated carbon (Anon., 1978; Suffet and McGuire, 1980; McGuire and Suffet, 1980), macroreticular resins (Symons et al., 1979), and ion exchange resins (Symons and Stevens 1979) as well as by biologically activated carbon (Kuhn and Sontheimer, 1979). Stevens and Symons (1977) demonstrated that adjustment of pH and the point of chlorination have a marked effect on trihalomethane production. Conventional treatment processes such as coagulation (Love et al., 1976) and lime softening (Singley, 1977; Wood, 1978) also remove some of the precursor material, whereas aeration (Love et al., 1976) as predicted was shown to be ineffective. Once trihalomethanes are formed several treatment processes are possible such as aeration (Kavanaugh and Trussell, 1980) carbon absorption (Cotruvo and Sontheimer, 1979) or macroreticular resin absorption (Symons 1978). Oxidation by ozonation or chlorine dioxide (Symons et al., 1979) has been

shown to have no effect on trihalomethane removal.

A comprehensive understanding of the variables affecting the formation and distribution of trihalomethanes could provide the information necessary to make decisions concerning cost effective control techniques.

A. Mechanism of Trihalomethane Formation: The formation of trihalomethanes during the chlorination of drinking water results from two important reactions, one is similar to the classic haloform reaction and the second is the oxidative opening of phenolic or other aromatic compounds (Boyce et al., 1981; Gould and Fitchora, 1981). Figure 2.1 shows the classical reaction sequence for the formation of haloforms (Morris and Baum, 1977).

Factors affecting the reaction are bromide, pH, reaction time, temperature, and chlorine dose. Ammonia also affects the reaction by competing for chlorine. It is important to note that these parameters are not independent of each other and when present together competing reactions complicate the overall reaction.

B. Effect of Bromide: The effect of bromide ion is extremely important in the formation and distribution of trihalomethanes during aqueous chlorination. Bromide is quantitatively oxidized by chlorine (HOCl or OCl^-) to HOBr/OBr^- and is very reactive in electrophilic substitution and addition reactions (Johnson and Inman, 1978), thus, this may affect both the rate of the overall reaction as well as the distribution of products (Rook, 1978; Minear, 1981).

The effect of bromide ion on the formation of bromine-containing THM's have been shown by several studies (Bunn, et al., 1975; Trussell and Umphres, 1978) where direct additions of bromide yielded changes

THE HALOFORM REACTION

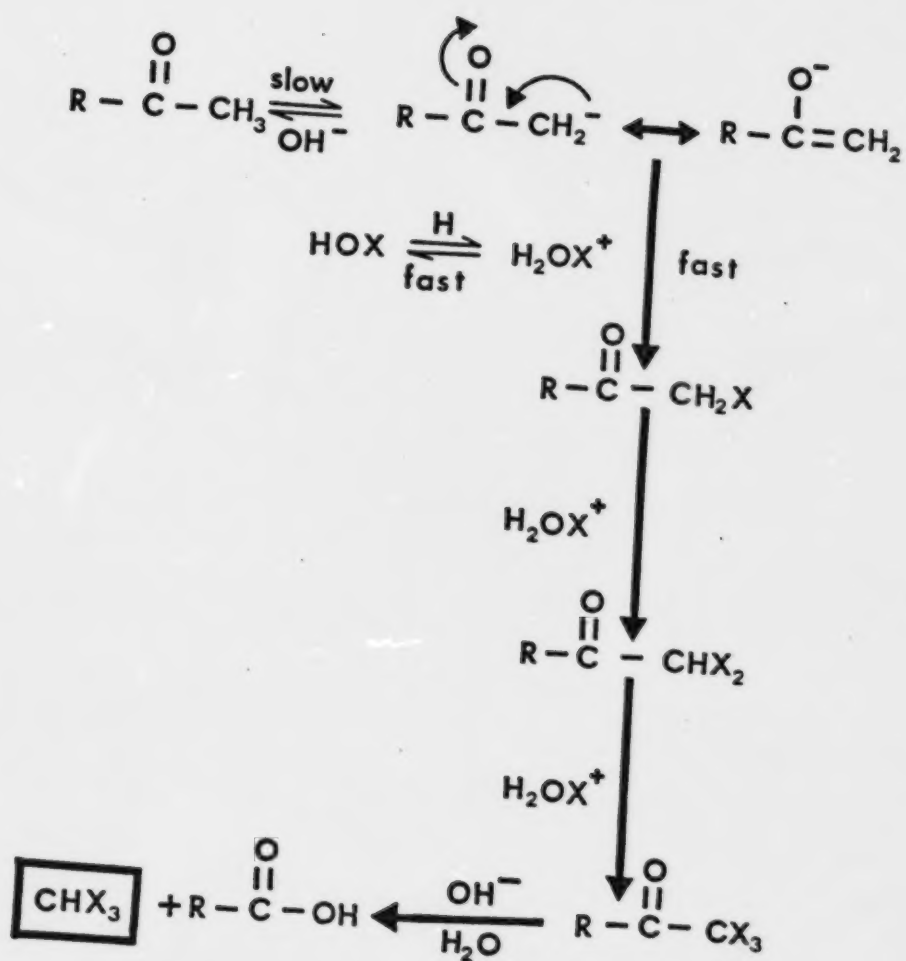


Fig. 2.1. The haloform reaction. (Morris and Baum, 1977)

in the THM distribution (Caruo and Stevenson, 1978). Also Lange and Kawczynski (1978) reported an increase in THM concentrations during the time of treatment at a water treatment plant in Contra Costa, California, when sea water was temporarily responsible for an increase in bromide concentrations. Luong et al. (1980, 1981) demonstrated that the increased formation of more highly brominated trihalomethanes is dependent primarily by the bromide concentration although total organic carbon and chlorine also are important parameters in determining the overall balance of THM's produced.

Several studies involving bromide ion have shown that as the bromide ion is increased, all other conditions being equal, there is a net increase in the total amount of THM's produced (Bird, 19790; Minear, 1980, 1981; Minear and Bird, 1980). A substantial reduction in chloroform concentration was observed with increasing amounts of bromodichloromethane, chlorodibromomethane and bromoform. At very high bromide concentration, bromoform was the major species present accounting for nearly 80% of overall THM formation. Consequently, while the influence of bromide was to increase the total moles of THM's formed, the shift to brominated species with higher molecular weight further increases the yield on a mass per volume basis (Minear, 1981).

Oliver (1980) has stated "after three weeks reaction time, THM yields (on a molar basis) in bromide solutions are only slightly larger than after 24 hours. The implication is that bromide reactions are faster, but chlorine reactions eventually go to completion." Cooper et al. (1981) reported that the presence of Br^- significantly affects both the distribution and concentration of THM's formed. They concluded that at very low concentrations, 1×10^{-6}

mol/L, very little effect was observed. At the higher concentrations, 1×10^{-5} mol/L to 1×10^{-4} mol/L, an effect was observed in the distribution of the THM's. They reported also that the total concentration of THM's formed (on a molar basis) were not influenced to any great extent by the addition of Br^- .

Minear (1981) demonstrated that the influence of bromide coupled with other variables is not a simple effect. The bromide level influences both the magnitude of the variation and the distribution in THM production.

Minear (1981) also demonstrated changes in the raw water bromide with time on his study in Tennessee. Veenstra and Schnoor (1980) showed this for the Iowa River where the relative composition of THM's varied seasonally in concert with changes in the relative contributions of surface and ground water to the river flow.

C. Effect of Time: Symons et al. (1981) demonstrated that the formation of trihalomethanes under natural conditions is not instantaneous, although, under some circumstances the formation of trihalomethanes may be complete in less than an hour. Engerholm (1981) in relation to time considerations, reported that THM yields from a raw water source have been shown to vary from one season to another. This seasonal variation has been attributed in many studies the change in the water temperature and, in some cases, to seasonal changes in precursor concentration and composition.

D. Effect of Temperature: Stevens et al. (1976) reported that increasing the temperature has a positive effect on trihalomethane formation. Brett and Calvery (1979) reported that the rate of formation of THM's was greater in summer than in winter. Veenstra and

Schnoor (1980) in a study of the Iowa River over a one-year time found lower THM's in the winter than in the summer, but did not attribute to changes in TOC concentration. Similarly, Symons et al. (1980) reported a seasonal variation at a water utility using the same source.

E. Effect of pH: As pH is increased the pH yield and rate of formation of THM's is increased. The increase in trihalomethane formation rate with pH is expected, because the classic haloform reaction is base-catalyzed (Symons et al. 1980). Christman (1977) suggested another explanation for the effect of pH on the rate and yield with the humic acid precursor involving the "opening up" of the natural humics structure by mutual repulsion of the negative charges at high pH thus increasing the availability of reactive sites.

F. Effect of Total Organic Carbon: Oliver and Lawrence (1979), found a linear correlation between the TOC and total trihalomethane yield. Several researchers have reported a linear relationship between chloroform yield and the TOC of the water (Rook, 1976; Stevens et al., 1976; Babcock and Singer, 1979; Kavanaugh et al., 1980).

Symons et al. (1980) demonstrated that an increase in the concentration of humic acid precursor (TOC) in the presence of excess chlorine (other reaction conditions being constant) caused trihalomethane yields to increase in direct proportion to the humic acid concentration.

G. Effect of Chlorine Concentration: There has been considerable controversy as to the actual effect of the chlorine concentration on the rate of trihalomethane formation. Symons et al. (1981) reported that where precursor is kept constant, only a slight influence on

trihalomethane formation rate or yield occurs when the free chlorine dose is increased beyond the demand. Several studies (Lange and Kawczynski, 1978; Trussell, 1978; Trussell and Umphres, 1978) showed that once the chlorine demand was satisfied, increasing chlorine residual concentration had little influence on trihalomethane yield.

Contrary results have been reported by Rook (1976) and by Kavanaugh and Trussell (1980) while conducting tests with different sources of precursor. Kavanaugh et al. (1980) concluded that the rate of THM formation depended strongly on the applied chlorine dose, with an increase as the chlorine concentration increased.

H. The Effect of Ammonia: In aqueous solution, free chlorine reacts with ammonia as shown in Figure 2.2. These reactions represent the most recent model of the chlorination breakpoint phenomena and are shown pictorially in Figure 2.3. Breakpoint chlorination occurs when sufficient chlorine has been added to water to convert the ammonia in solution to nitrogen gas and other end products. Before the breakpoint the chlorine residuals are chloramines. After breakpoint a mixture of hypochlorous acid (HOCl) and hypochlorite ion (OCl^-) is present. A minor concentration of NCl_3 may be present.

The rate of the reaction of chlorine with ammonia is several orders of magnitude faster than for trihalomethane formation. Once formed, chloramines apparently do not react with organics to form THM's (Symons, 1980). Thus, the formation of THM's is effected by the presence of ammonia.

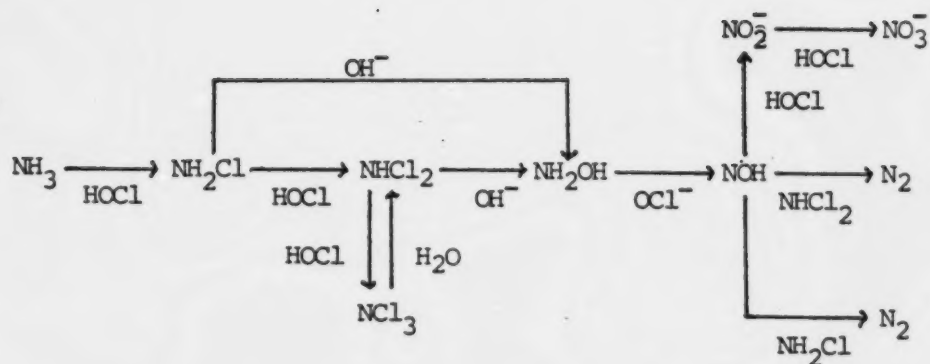


Fig. 2.2. Proposed reaction scheme of chlorine and ammonia in water.
(Saunier and Selleck, 1979)

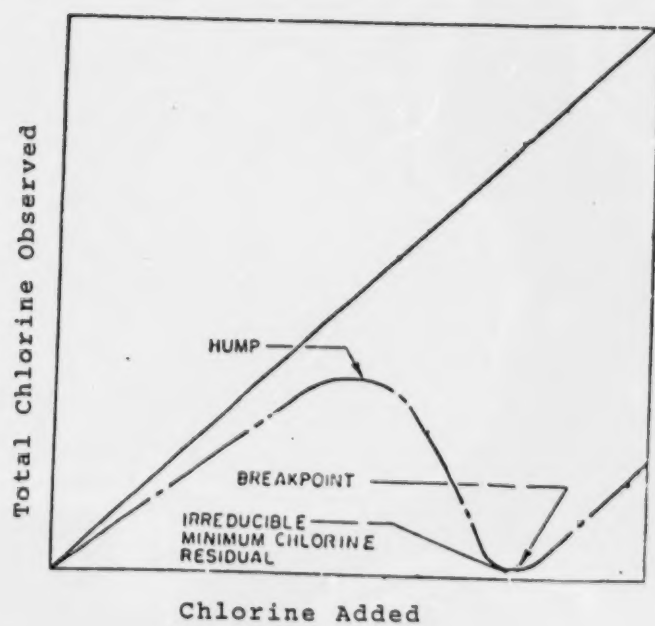


Fig. 2.3. Breakpoint chlorination curve.

III. EXPERIMENTAL METHODS AND MATERIALS

A. Water Characterization: The study was conducted on ground water obtained from the Preston Water Treatment Plant, well number four, Hialeah, Florida. The water samples were characterized according to Standard Methods (1975). Table 3.1 lists the tests conducted on each water sample.

B. Chlorine Solution: Sodium hypochlorite, laboratory grade, (Fisher Scientific Company, Lot 702283-12) was used throughout. The concentration of sodium hypochlorite solution was determined using iodometric titration.

C. Iodometric Titration: The titrimetric method used was the Iodometric Method 1, 409A of Standard Methods (1975). Minor changes were made in the normality of reagents.

D. FACTS: The FACTS procedure was used to determine free chlorine (Cooper et al., 1975; Standard Method 1975). The chemical basis for this test is the oxidation of syringaldazine to a colored product, $\lambda_{\max} = 530 \text{ nm}$. The test was used as a qualitative tool (Ames Chemical Co., Elkhart, IN).

E. Breakpoint Curves: Breakpoint curves were developed for each sample of ground water. The curve was used to find out the exact break point and to determine the chlorine concentrations used in the study. The procedure for determining the breakpoint curve involved setting up twenty Erlenmeyer flasks (numbered) and adding, 200 mL of unbuffered ground water to each flask. Chlorine solution, (NaOCl) was

TABLE 3.1
TESTS PERFORMED FOR CHARACTERIZATION OF GROUND WATER

Test	Method
Alkalinity	403, p278*
Hardness	309B, p202*
Cl ⁻	Ion Chromatography
SO ₄ ⁻²	
NH ₃ - N (Nesslerization)	418B, p412*
pH	Electrode
TOC	Dohrman DC-54

* Standard Methods, 1975

added to each Erlenmeyer in increments of 2 mg/L Cl_2 , the flask covered with parafilm and swirled to mix. The samples were stored in the dark for two hours and checked for the presence of free chlorine, using the FACTS procedure, to determine if break point had been reached. Each sample was then titrated with NaS_2O_3 and the total chlorine concentration calculated in mg/L as Cl_2 . These Cl_2 concentrations were plotted, mg/L Cl_2 added as a function of mg/L Cl_2 observed.

F. Preparation of Serum Vials: Sixty milliliter serum vials (Wheaton Scientific, 223745) were used to determine the formation of trihalomethanes. These vials were washed with low sudsing laboratory detergent for 15 minutes at a water temperature of 150°C, rinsed repeatedly with tap and then distilled water. After washing, the vials were dried at 110°C overnight. Septa for the vials were silicone rubber with a Teflon® face (Wheaton Scientific, 224173) which were sealed with aluminum caps (Wheaton Scientific, 224193).

G. Chlorination of Ground Water: After the breakpoint curve was determined six chlorine concentrations were chosen for study. Three concentrations before the break point, two after the break point and one at break point. For each sample of ground water, the chlorine concentrations after break point were chlorine to TOC ratios of 4:1 and 6:1.

Prior to chlorination the pH was adjusted to either pH 7 by adding 1.6802 grams of analytical grade sodium bicarbonate or to pH 9 by adding 7.6270 grams of analytical grade sodium borate, to two liters of ground water.

The experimental solutions were chlorinated with the standardized chlorine solution. A control sample was sealed in a 60 mL serum vial using a teflon lined septum. After chlorination, the test solutions were sealed in serum vials with Teflon® septa and aluminum crimp seals and kept at room temperature, 25°C. The vials were stored in the dark, at room temperature during the reaction period. At the end of each designated reaction time an excess of sodium thiosulfate, 0.35 grams, was added to the vials to terminate the trihalomethane reactions. The vials were then stored in the refrigerator until trihalomethane analyses were performed.

Eight reaction times, 1, 2, 4, 8, 24, 48, 96 and 144 hours were used for this study.

To study the effect of bromide, three concentrations of bromide (1×10^{-6} , 1×10^{-5} and 1×10^{-4} mol/L) were used. The bromide (infrared grade) was added as a powder in the case of the 1×10^{-4} mol/L concentration and as a solution in the case of 1×10^{-5} mol/L and 1×10^{-6} mol/L concentrations.

H. Determination of Trihalomethanes Concentration: Trihalomethanes (THM's) were determined by the purge and trap procedure reported by Bellar and Lichtenberg (1974). Trihalomethanes were purged by helium gas bubbled through the aqueous samples. The trihalomethanes, along with other organic constituents that exhibit low water solubility and a vapor pressure significantly greater than water, were efficiently transferred from the aqueous phase to the gaseous phase. These compounds were swept from the purging device and were trapped in a

short column containing Tenax® GC sorbent. After a purging time of 11 minutes, the trapped components were thermally desorbed and back flushed in six minutes at 225°C onto a cold, 2.4 m x 0.32 cm O.D. Tenax® gas chromatographic column.

The gas chromatograph used throughout was a Tracor 560, adapted for dual column determination using two tracor 700 Hall Electrolytic Conductivity detectors. The chromatographic program held the column 95°C for 14 minutes, then increased the temperature to 220°C at a rate of 4°C/min. Areas under peaks were obtained using Hewlett Packard 3390 integrators, one for each detector.

The concentration of trihalomethanes in the experimental samples was determined by comparing the peak height of the sample with the peak heights of known standards. Three standard samples of different concentrations were run every day and a least squares linear regression fit of the data was used as the standard curve. Each sample was run in triplicate and the 95 percent confidence interval determined.

I. Ammonia Removal Mini-Column: During preliminary research it was observed that ammonia not only interfered with the chromatographic determination of organohalogen compounds, but also had an adverse effect on Tenax® GC columns. Ammonia is released when chloramines are reduced, and because many of the samples to be tested were before the breakpoint, it was necessary that a technique to remove ammonia before chromatographic analysis of the trihalomethanes.

Pasteur pipettes (14.5 cm x 0.7 cm) were used to make mini-ion

exchange columns for ammonia removal. A glass wood plug, 1 cm, was inserted in the top and pushed through to the beginning of the narrow base. Rohm and Haas Amerlite® IRN 150 Tech ion exchange resin was added to a column length of 6 cm and the pipette stopped with a septum (7.0 mm x 10 mm). Before use, the column was flushed with a minimum of 20 mL of helium purged distilled water.

Standards and samples were passed through the mini-column in a similar manner. A sample to be tested was withdrawn into a glass 5 mL syringe, injected and was passed through the column directly into the purge and trap apparatus. The exact amount of the sample used was dependent on the concentration of the unknown, i.e., where high concentrations of organohalogen compounds were found a volume less than five mL was used. For low concentrations of trihalomethanes, larger volumes were used employing larger purging apparatus (Cooper et al., 1982b).

Experiments were conducted at both pH 7 and 9. To insure adequate removal of the NH_3 , the pH of all solutions were lowered to pH 5 by the addition of KH_2PO_4 .

IV. EXPERIMENTAL RESULTS

In this chapter the results of the research on the formation and distribution of trihalomethanes in chlorinated ground water are presented.

Water quality analyses and trihalomethane analyses were conducted on ground water sample designated A (July 14, 1981), B (October 30, 1981), C (December 3, 1981) and D (August 25, 1981). The ground water samples were obtained from the Biscayne aquifer at the John E. Preston Water Treatment Plant, well number four, Hialeah, Florida.

From the results in Table 4.1 it can be seen that the water quality with respect to the parameters tested, did not change significantly throughout the period of the experiment. No significant change appeared in the background concentration of trihalomethane in the ground water samples (Table 4.2). It is also apparent that the organic carbon concentration (TOC) did not change significantly for the duration of this study. Therefore, during the four phases of this research the quality of ground water remained relative constant.

To describe the formation and distribution of THM's during water treatment, the effect of the variables bromide, pH, reaction time and chlorine concentration were examined. Table 4.3 presents the experimental variables used in this study. The experimentation was conducted in four experimental phases represented by samples A, B, C and D. The only difference in each experiment was the concentration

TABLE 4.1

WATER QUALITY ANALYSIS OF SAMPLES OBTAINED FROM THE BISCAYNE AQUIFER,
PRESTON WATER TREATMENT PLANT WELL NO. 4, HIALEAH, FLORIDA.

Sample Date	A	B	C	D
Sample Designation	July 14, 1981	October 30, 1981	December 3, 1981	August 25, 1981
TOC (mg/L)	6.00	5.90	6.00	5.80
Alkalinity (mg/L as CaCO_3)	233	249	259	238
Hardness (mg/L as CaCO_3)	252	232	239	235
$\text{NH}_3 - \text{N}$ (mg/L)	2	2	2	2
SO_4^{-2} (mg/L)	30.6	28.1	26.5	29.0
Cl^- (mg/L)	46.2	43.1	41.3	46.0
pH	7.24	7.10	6.95	7.20

TABLE 4.2
 TRIHALOMETHANE ANALYSIS OF WATER SAMPLES OBTAINED FROM THE BISCAYNE AQUIFER,
 PRESTON WATER TREATMENT PLANT, WELL NO. 4, HIALEAH, FLORIDA.

Sample Designation	Trihalomethane								Total	
	CHCl ₃		CHCl ₂ Br		CHClBr ₂		CHBr ₃		THM	THM
	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹
July 14, 1981 A	4.10+1.25	34.4+10.5	2.10+0.56	12.8+3.4	1.70+1.08	8.14+5.17	2.10+0.39	8.32+1.54	10.0	63.7
August 25, 1981 D	4.00+1.48	33.5+12.4	2.00+0.19	12.2+1.2	1.65+0.31	7.90+1.48	2.15+1.08	8.51+4.28	9.80	62.1
October 30, 1981 B	3.95+0.55	33.1+4.6	2.00+1.15	12.2+7.0	1.85+0.25	8.86+1.20	2.10+0.77	8.32+3.05	9.90	62.5
December 3, 1981 C	3.55+1.88	29.7+15.8	1.85+0.95	11.3+5.8	1.63+1.15	7.81+5.51	1.95+1.01	7.72+4.00	8.98	56.5

TABLE 4.3

EXPERIMENTAL VARIABLES FOR STUDYING THE FORMATION AND DISTRIBUTION
OF TRIHALOMETHANES IN CHLORINATED GROUND WATER.

Variables	
Bromide	1×10^{-6} mol/L, 1×10^{-5} mol/L and 1×10^{-4} mol/L
Chlorine	6 concentrations (included Cl ₂ : TOC of 4:1 and 6:1)
pH	7,9
Time (hours)	0,1,2,4,8,24,48,96 and 144

Note: All experiments were conducted at 24 C.

of Br^- added to the groundwater sample.

A. Breakpoint Data: Breakpoint curves were determined for groundwater samples A, B, C and D. The breakpoint curves were used to determine the exact point of the break point (minimum chlorine residual) and the chlorine concentrations for the study, and were obtained prior to the addition of Br^- to the sample. Figures 4.1, 4.2, 4.3, and 4.4 present the breakpoint curves. Tables 4.4, 4.5, 4.6 and 4.7 present the data obtained for the breakpoint curves of the groundwater samples.

During each experimental phase of this research, six chlorine concentrations were selected from the breakpoint curves, as shown in Figures 4.1, 4.2, 4.3 and 4.4 and summarized in Table 4.8.

B. Facts Test Results: At each reaction time, the FACTS procedure was used to determine the presence of free residual chlorine, Tables 4.9, 4.10, 4.11 and 4.12 present a summary of the data obtained. In the samples to which Br^- was added the FACTS test would also record a positive for HOBr/OBr^- and bromamines (Ryan, 1979).

The results for experiments A and B, with no Br^- added and 1×10^{-6} mol/L Br^- , respectively, were identical. No free residual was observed at any reaction time, for either pH 7 or 9, before or at the break point, i.e. chlorine concentrations 1 through 4. A free-residual was observed at all reaction times at both pH's after break point, i.e. chlorine concentration 5 and 6. In experiments C and D only chlorine concentration 5 showed a difference in the free residual reading. Chlorine concentrations 1 through 4 showed no

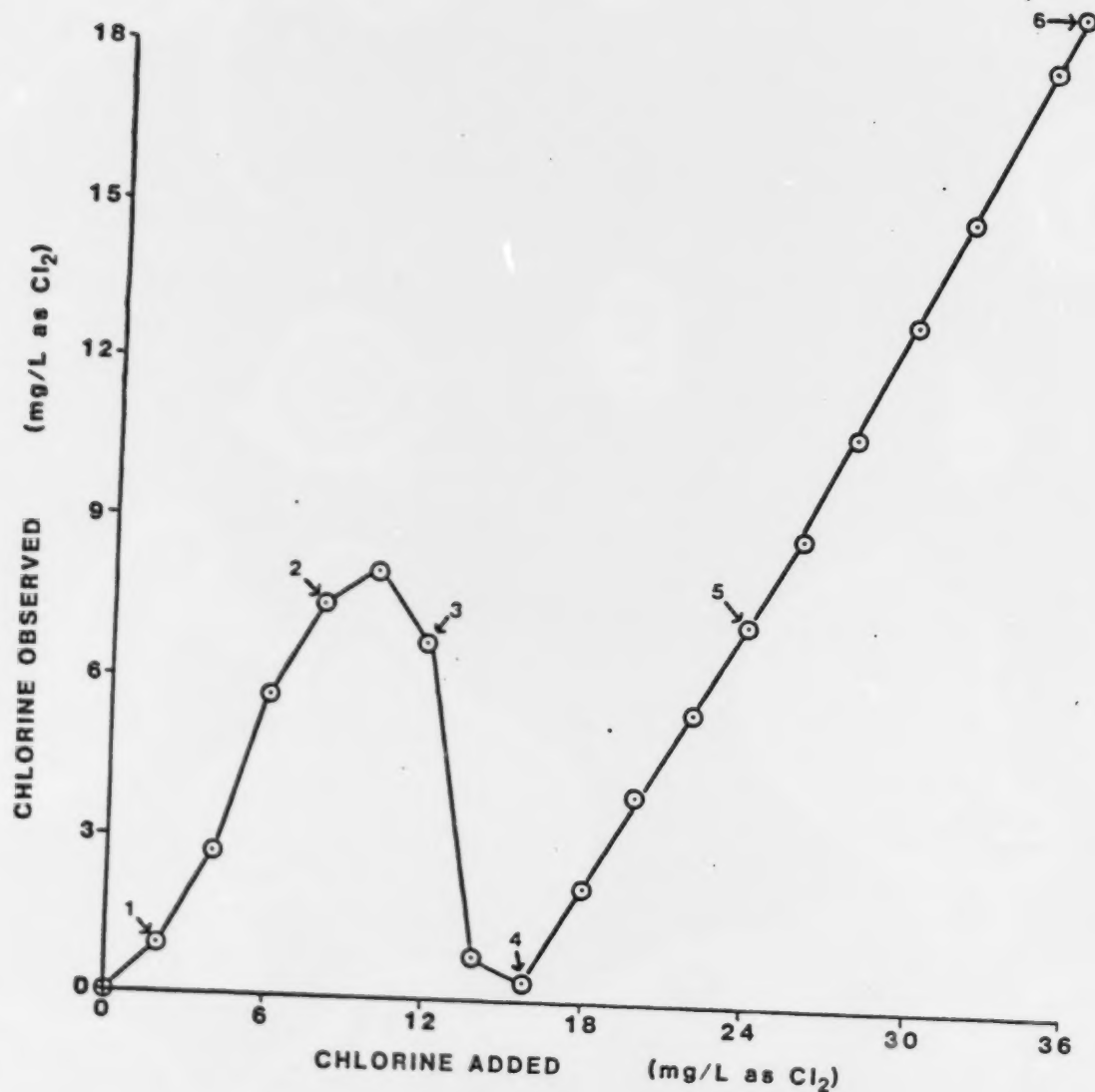


Fig. 4.1. Breakpoint chlorination curve of ground water obtained from the Biscayne Aquifer, at the Preston water treatment plant, Miami, FL., Phase A.

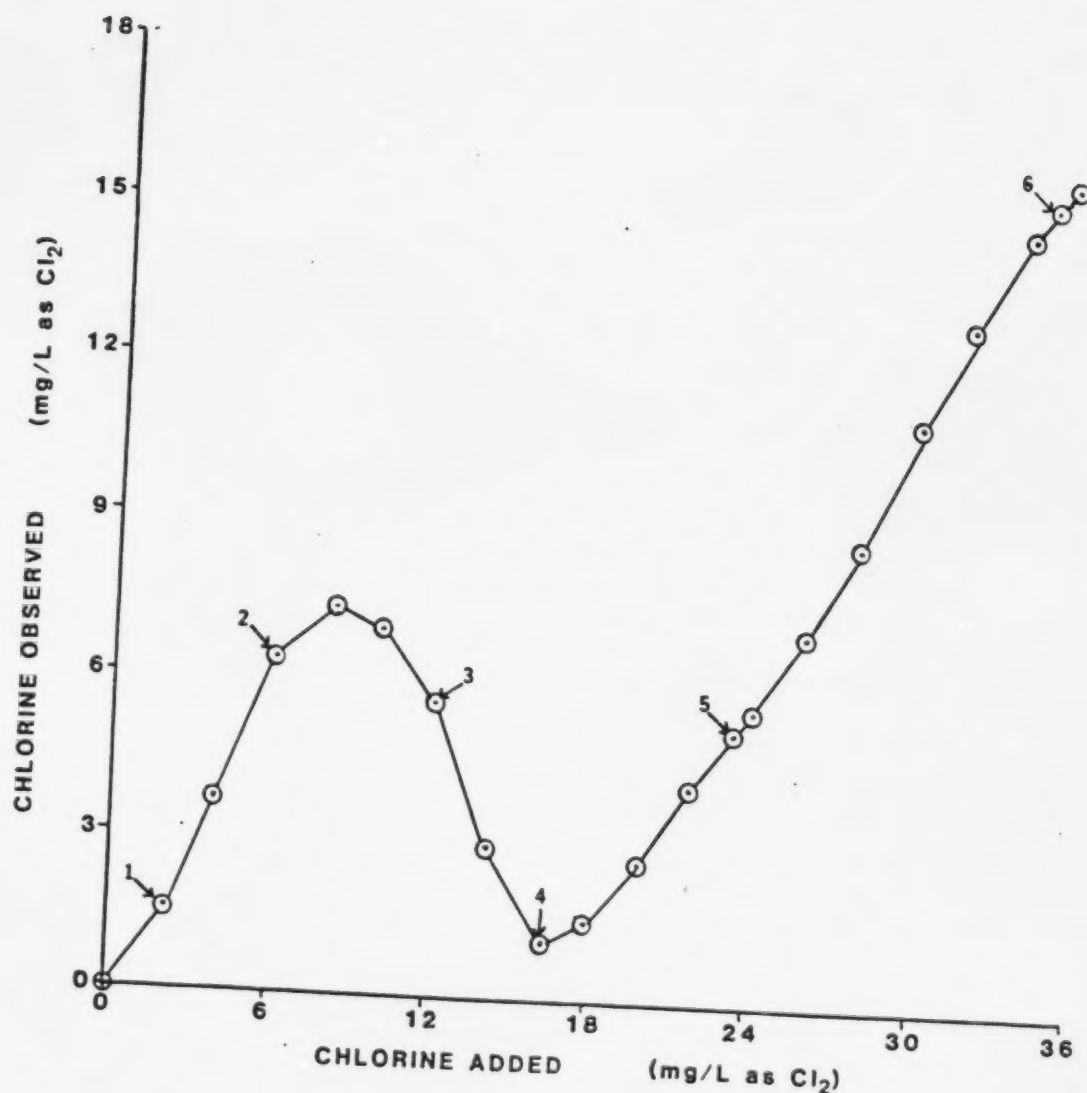


Fig. 4.2. Breakpoint chlorination curve of ground water obtained from the Biscayne Aquifer, at the Preston water treatment plant, Miami, FL., Phase B.

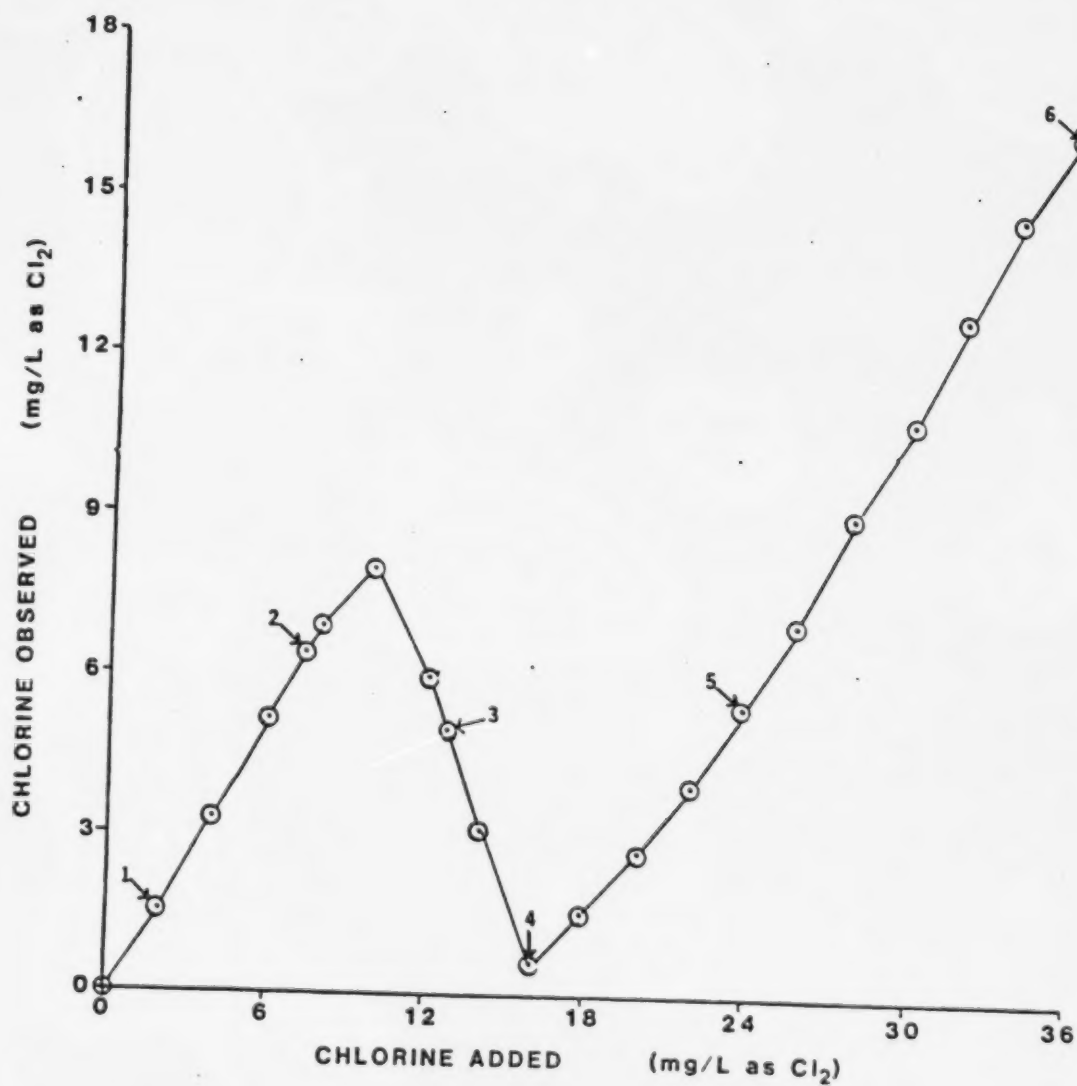


Fig. 4.3. Breakpoint chlorination curve of ground water obtained from the Biscayne Aquifer, at the Preston water treatment plant, Miami, FL., Phase C.

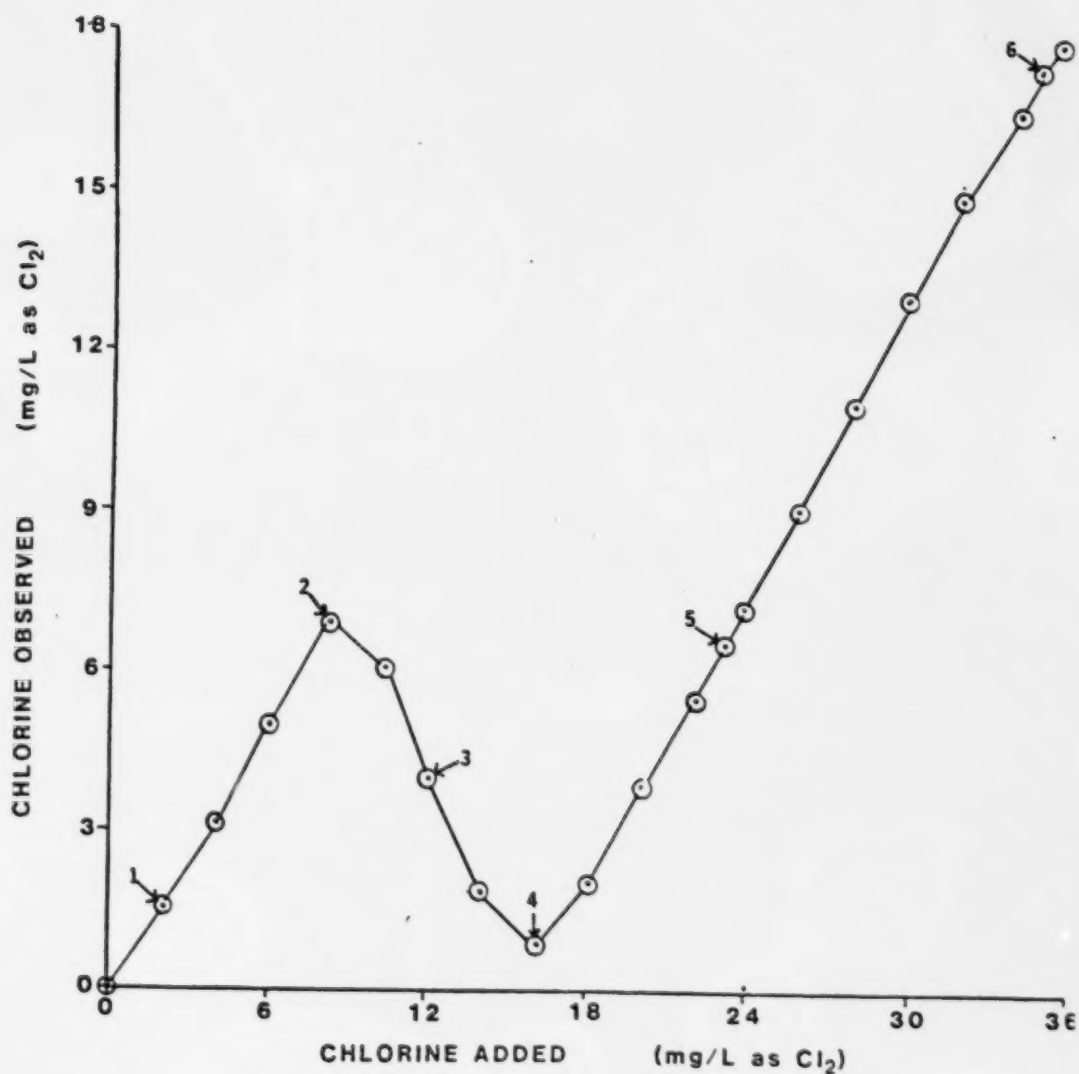


Fig. 4.4. Breakpoint chlorination curve of ground water obtained from the Biscayne Aquifer, at the Preston water treatment plant, Miami, FL., Phase D.

TABLE 4.4
BREAKPOINT DATA FOR GROUNDWATER SAMPLE A OBTAINED ON JULY 14, 1981

Experimental phase A.

Number	Chlorine added (mg/L as Cl ₂)	Chlorine observed (mg/L as Cl ₂)	Cl ₂ : TOC
1	-	-	-
2	2*	0.91	0.33:1
3	4	2.90	0.67:1
4	6	5.61	1.00:1
5	8*	7.42	1.33:1
6	10	7.96	1.67:1
7	12*	6.34	2.00:1
8	14	0.54	2.33:1
9	16*	0.38	2.66:1
10	18	2.44	3.00:1
11	20	3.44	3.33:1
12	22	5.79	3.66:1
13	24*	7.42	4.00:1
14	26	8.83	4.33:1
15	28	10.9	4.66:2
16	30	13.0	5.00:1
17	32	15.3	5.33:1
18	34	18.2	5.67:1
19	36*	19.1	6.00:1

*Chlorine concentration chosen for experiment

TABLE 4.5
BREAKPOINT DATA FOR GROUNDWATER SAMPLE B OBTAINED ON OCTOBER 30, 1981
Experimental phase B.

Number	Chlorine added (mg/L as Cl ₂)	Chlorine observed (mg/L as Cl ₂)	Cl ₂ : TOC
1	-	-	-
2	2*	1.71	0.34:1
3	4	4.28	0.68:1
4	6*	6.67	1.02:1
5	8	7.18	1.36:1
6	10	6.84	1.69:1
7	12*	5.30	2.03:1
8	14	2.05	2.37:1
9	16*	1.05	2.71:1
10	18	1.37	3.05:1
11	20	2.91	3.39:1
12	22	4.62	3.73:1
13	23.6*	5.61	4.00:1
14	24	6.16	4.07:1
15	26	7.87	4.41:1
16	28	10.3	4.75:1
17	30	13.0	5.08:1
18	32	14.0	5.42:1
19	34	15.0	5.76:1
20	35.4*	15.5	6.00:1
21	36	16.2	6.10:1

*Chlorine concentration chosen for experiment

TABLE 4.6

BREAKPOINT DATA FOR GROUNDWATER SAMPLE C OBTAINED ON DECEMBER 3, 1981

Experimental phase C.

Number	Chlorine added (mg/L as Cl ₂)	Chlorine observed (mg/L as Cl ₂)	Cl ₂ : TOC
1	-	-	-
2	2*	1.74	0.33:1
3	4	3.25	0.67:1
4	6	5.27	1.00:1
5	7.50*	6.49	1.25:1
6	8	7.04	1.33:1
7	10	8.05	1.67:1
8	12	6.24	2.00:1
9	13*	5.35	2.17:1
10	14	3.24	2.33:1
11	16*	0.64	2.66:1
12	18	1.69	3.00:1
13	20	2.13	3.33:1
14	22	3.76	3.66:1
15	24*	5.47	4.00:1
16	26	7.49	4.33:1
17	28	9.66	4.66:1
18	30	11.0	5.00:1
19	32	13.7	5.33:1
20	34	15.0	5.67:1
21	36*	16.1	6.00:1

*Chlorine concentration chosen for experiment

TABLE 4.7

BREAKPOINT DATA FOR GROUNDWATER SAMPLE D OBTAINED ON AUGUST 25, 1981

Experimental phase D.

Number	Chlorine added (mg/L as Cl ₂)	Chlorine observed (mg/L as Cl ₂)	Cl ₂ : TOC
1	-	-	-
2	2*	1.75	0.34:1
3	4	3.39	0.69:1
4	6	4.95	1.03:1
5	8*	7.25	1.33:1
6	10	6.37	1.72:1
7	12*	3.89	2.07:1
8	14	1.50	2.41:1
9	16*	0.89	2.76:1
10	18	2.21	3.10:1
11	20	3.72	3.45:1
12	22	6.73	3:79:1
13	23.2*	6.98	4.00:1
14	24	7.61	4.14:1
15	26	9.56	4.48:1
16	28	12.0	4.83:1
17	30	13.5	5.17:1
18	32	14.2	5.52:1
19	34	15.9	5.86:1
20	38*	17.4	6.00:1
21	36	18.1	6.21:1

*Chlorine concentration chosen for experiment

TABLE 4.8

SUMMARY OF CHLORINE CONCENTRATION CHOSEN ON BREAKPOINT CURVE FOR
GROUNDWATER SAMPLES (EXPERIMENTAL PHASES) A, B, C AND D.

Chlorine concentration number	Chlorine added (mg/L as Cl ₂)	Chlorine observed (mg/L as Cl ₂)	Cl ₂ : TOC
Sample A			
1	2	0.91	0.33:1
2	8	7.42	1.33:1
3	12	6.34	2.00:1
4	16	0.38	2.66:1
5	24	7.42	4.00:1
6	36	19.1	6.00:1
Sample B			
1	2	1.71	0.34:1
2	6	6.67	1.02:1
3	12	5.30	2.03:1
4	16	1.05	2.71:1
5	23.6	5.61	4.00:1
6	35.4	15.5	6.00:1
Sample C			
1	2	1.74	0.33:1
2	7.50	6.49	1.25:1
3	13	5.35	2.17:1
4	16	0.64	2.66:1
5	24	5.47	4.00:1
6	36	16.1	6.00:1
Sample D			
1	2	1.75	0.34:1
2	8	7.25	1.33:1
3	12	3.89	2.07:1
4	16	0.89	2.76:1
5	23.2	6.98	4.00:1
6	34.8	17.4	6.00:1

TABLE 4.9

SUMMARY OF THE RESULTS OBTAINED USING THE FACTS TEST FOR DETERMINING FREE RESIDUAL CHLORINE IN CHLORINATED GROUNDWATER SAMPLE (EXPERIMENTAL PHASE) A. NO Br^- ADDED AS A FUNCTION OF CHLORINE CONCENTRATION, pH, AND REACTION TIME.*

Chlorine Concentration Number	pH	Reaction time (hours)							
		1	2	4	8	24	48	96	144
1	7	-	-	-	-	-	-	-	-
	9	-	-	-	-	-	-	-	-
2	7	-	-	-	-	-	-	-	-
	9	-	-	-	-	-	-	-	-
3	7	-	-	-	-	-	-	-	-
	9	-	-	-	-	-	-	-	-
4	7	-	-	-	-	-	-	-	-
	9	-	-	-	-	-	-	-	-
5	7	+	+	+	+	+	+	+	+
	9	+	+	+	+	+	+	+	+
6	7	+	+	+	+	+	+	+	+
	9	+	+	+	+	+	+	+	+

* The symbol (-) denotes the absence of free chlorine and (+) denotes the presence of free chlorine.

TABLE 4.10

SUMMARY OF THE RESULTS OBTAINED USING THE FACTS TEST FOR DETERMINING FREE RESIDUAL CHLORINE IN CHLORINATED GROUNDWATER SAMPLE (EXPERIMENTAL PHASE) B (OCTOBER 30, 1981) 1×10^{-6} mol/L Br^- ADDED, AS A FUNCTION OF CHLORINE CONCENTRATION, pH, AND REACTION TIME.*

Chlorine Concentration Number	pH	Reaction time (hours)							
		1	2	4	8	24	48	96	144
1	7	-	-	-	-	-	-	-	-
	9	-	-	-	-	-	-	-	-
2	7	-	-	-	-	-	-	-	-
	9	-	-	-	-	-	-	-	-
3	7	-	-	-	-	-	-	-	-
	9	-	-	-	-	-	-	-	-
4	7	-	-	-	-	-	-	-	-
	9	-	-	-	-	-	-	-	-
5	7	+	+	+	+	+	+	+	+
	9	+	+	+	+	+	+	+	+
6	7	+	+	+	+	+	+	+	+
	9	+	+	+	+	+	+	+	+

* The symbol (-) denotes the absence of free chlorine and (+) denotes the presence of free chlorine.

TABLE 4.11

SUMMARY OF THE RESULTS OBTAINED USING THE FACTS TEST FOR DETERMINING FREE RESIDUAL CHLORINE IN CHLORINATED GROUNDWATER SAMPLE (EXPERIMENTAL PHASE) C (DECEMBER 3, 1981) 1×10^{-5} mol/L Br^- ADDED AS A FUNCTION OF CHLORINE CONCENTRATION, pH, AND REACTION TIME.*

Chlorine Concentration Number	pH	Reaction time (hours)							
		1	2	4	8	24	48	96	144
1	7	-	-	-	-	-	-	-	-
	9	-	-	-	-	-	-	-	-
2	7	-	-	-	-	-	-	-	-
	9	-	-	-	-	-	-	-	-
3	7	-	-	-	-	-	-	-	-
	9	-	-	-	-	-	-	-	-
4	7	-	-	-	-	-	-	-	-
	9	-	-	-	-	-	-	-	-
5	7	+	+	+	+	+	+	+	-
	9	+	+	+	+	+	+	-	-
6	7	+	+	+	+	+	+	+	+
	9	+	+	+	+	+	+	+	+

* The symbol (-) denotes the absence of free chlorine and (+) denotes the presence of free chlorine.

TABLE 4.12

SUMMARY OF THE RESULTS OBTAINED USING THE FACTS TEST FOR DETERMINING FREE RESIDUAL CHLORINE IN CHLORINATED GROUNDWATER SAMPLE (EXPERIMENTAL PHASE) D (AUGUST 25, 1981) 1×10^{-4} mol/L Br^- ADDED AS A FUNCTION OF CHLORINE CONCENTRATION, pH, AND REACTION TIME.*

Chlorine Concentration Number	pH	Reaction time (hours)							
		1	2	4	8	24	48	96	144
1	7	-	-	-	-	-	-	-	-
	9	-	-	-	-	-	-	-	-
2	7	-	-	-	-	-	-	-	-
	9	-	-	-	-	-	-	-	-
3	7	-	-	-	-	-	-	-	-
	9	-	-	-	-	-	-	-	-
4	7	-	-	-	-	-	-	-	-
	9	-	-	-	-	-	-	-	-
5	7	+	+	-	-	-	-	-	-
	9	+	-	-	-	-	-	-	-
6	7	+	+	+	+	+	+	+	+
	9	+	+	+	+	+	+	+	+

* The symbol (-) denotes the absence of free chlorine and (+) denotes the presence of free chlorine.

free residual whereas chlorine concentration 6 showed a free residual at all reaction times.

Chlorine concentration 5 for experiment C, 1×10^{-5} mol/L Br^- , showed a residual through 96 hours at pH 7 and 48 hours at pH 9. This result is consistent with the fact that the overall reaction is faster at pH 9 than pH 7 and therefore no oxidant remained after 48 hours at pH 9, i.e. the oxidant reacted completely.

Chlorine concentration 5 for experiment D, 1×10^{-4} mol/L Br^- , showed a free residual through 2 hours at pH 7 and 1 hour at pH 9. This result is also consistent with the fact that the reaction is more rapid at pH 9 than 7. The additional results that are of interest relate to the concentration of Br^- . It has been shown that the attack on precursors by Br^+ is faster than Cl^+ . This fact is confirmed by the experiments at chlorine concentration 5 where the only difference is the Br^- concentration, C, 1×10^{-5} mol/L and D, 1×10^{-4} mol/L.

C. Trihalomethane Results: During the four experimental phases of this research, data were obtained on the formation of THM's. These experiments and the methods used for measuring the relevant parameters have been described above. Presented in Appendix A, B, C and D are a tabulation of all experimental data, organized according to the four experimental phases A, B, C and D.

Under typical circumstances, the halogenated compounds produced in chlorinated groundwater are dominated by the trihalomethanes, trichloromethane or chloroform (CHCl_3), bromodichloromethane (CHBrCl_2), chlorodibromomethane (CHClBr_2) and tribromomethane or

bromoform (CHBr_3). The arithmetic sum, in $\mu\text{g/L}$, of these four compounds concentration has been defined as "Total Trihalomethanes" and is reported in $\mu\text{g/L}$ for regulatory purposes.

Experimental Phase A: As stated previously the experimental design was divided into four phases with the bromide concentration being the determining factor. In experimental phase A no bromide was added to the groundwater. The formation and distribution of THM's was investigated as a function of time, pH and chlorine concentration. The chlorine concentrations used in phase A are given in Table 4.4 and shown in Figure 4.1. Chlorine concentrations 5 and 6 were chosen to provide a $\text{Cl}_2:\text{TOC}$ ratio of 4:1 and 6:1, respectively. The other chlorine concentrations were chosen based on the breakpoint curve and the relative location on the curve.

The concentration of CHCl_3 as a function of time and at six chlorine concentrations is shown in Figure 4.5 and 4.6, for pH 7 and 9, respectively.

Chloroform was shown to follow, in a general way, the shape of the breakpoint curve. The chloroform concentration at all chlorine concentrations increased from chlorine concentration 1 to 3, decreased at concentration 4 and increased at 5 and 6. At pH 9 the concentration of CHCl_3 was higher than the corresponding pH 7 value, the difference being most significant after the break point.

The overall rate of formation of chloroform, i.e. the slope of the curves in Figures 4.5 and 4.6, was similar at both pH levels. Chlorine concentration 1 was practically level, no increase in concentration with time. Chlorine concentrations 2, 3, 4 and 5 gave

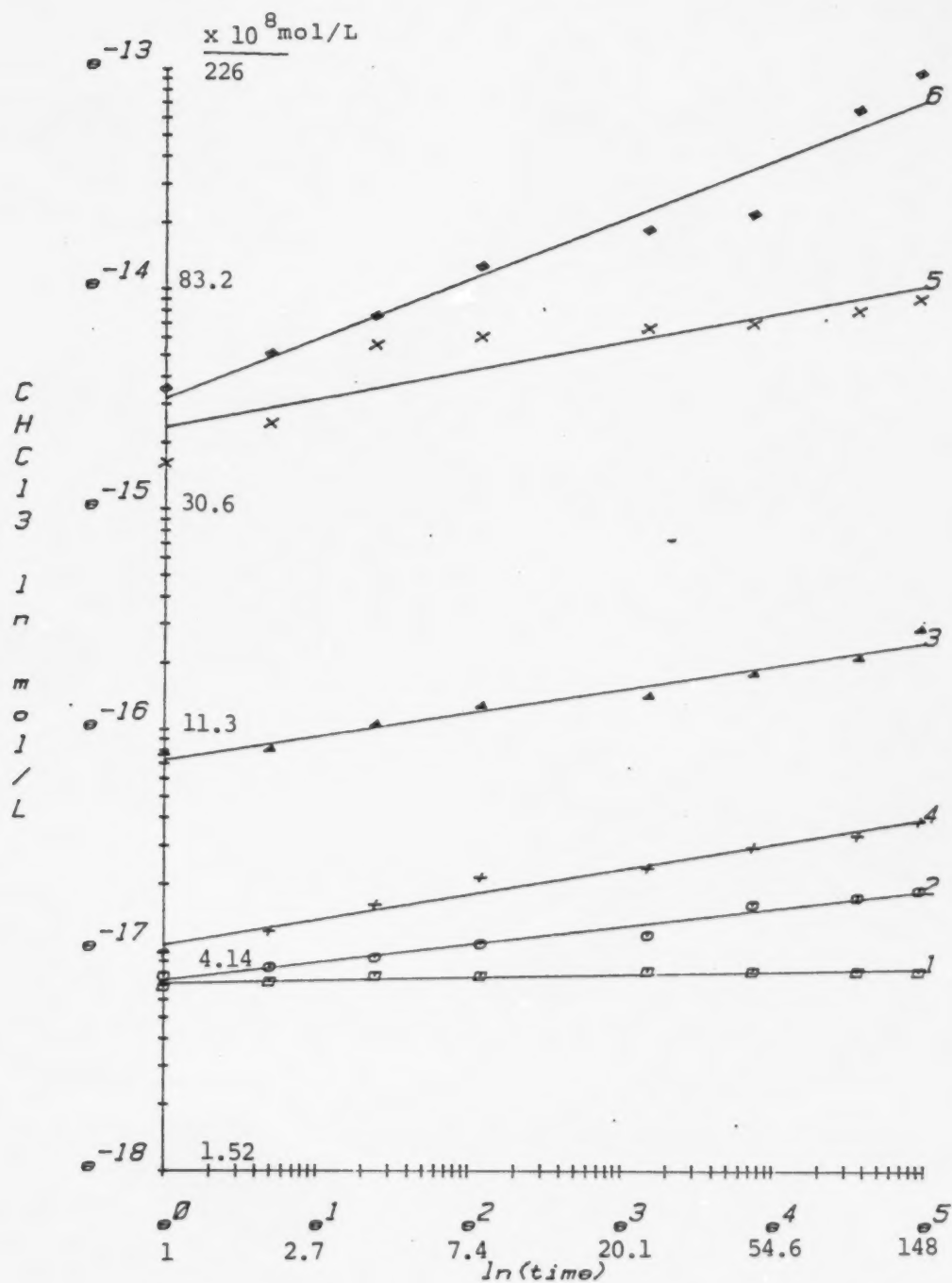


Fig. 4.5. CHCl_3 formation as a function of time at six chlorine concentrations (Phase A, No Bromide, pH 7).
(Time in hours.)

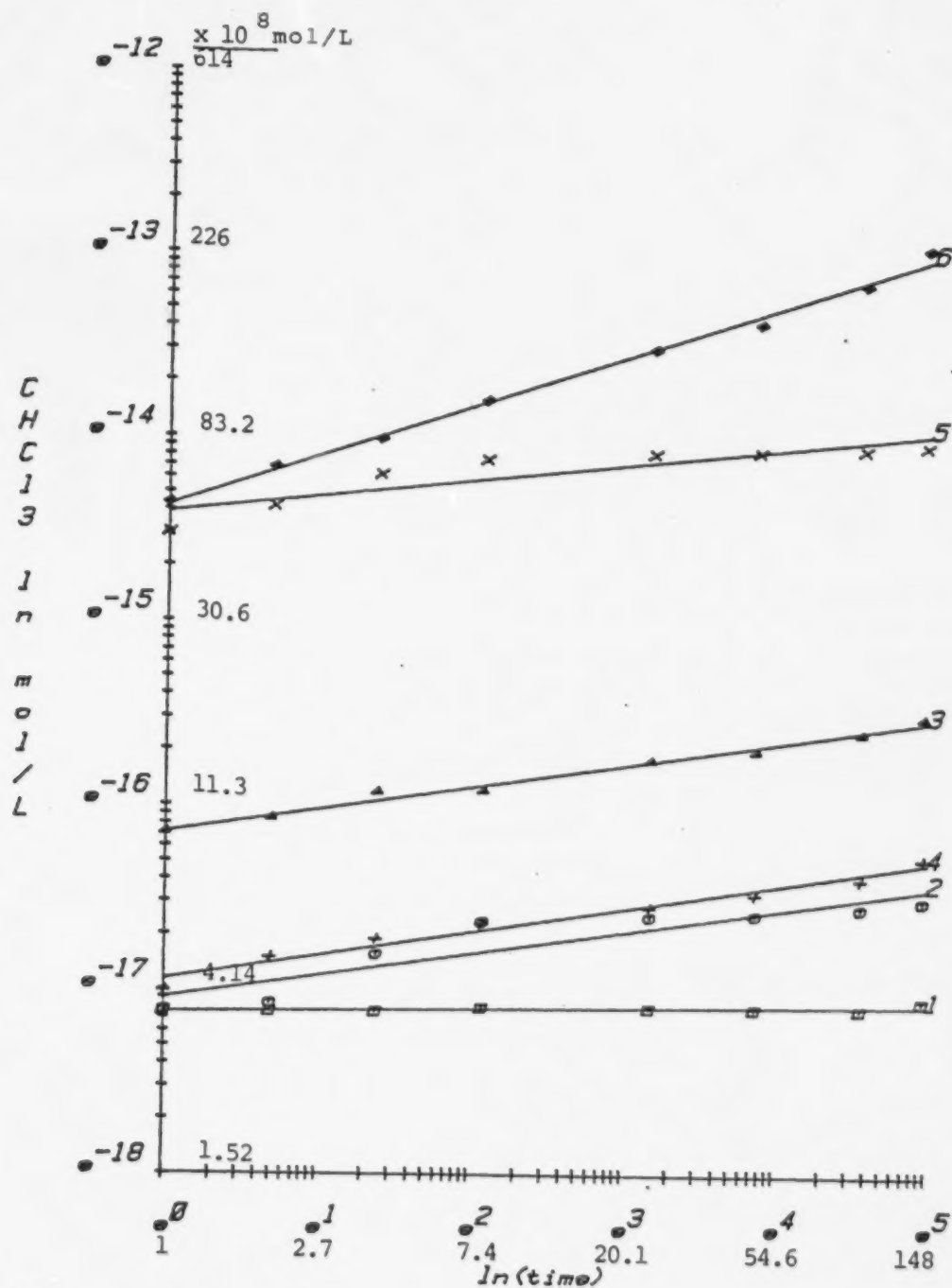


Fig. 4.6. CHCl_3 formation as a function of time at six chlorine concentrations (Phase A, No Bromide, pH 9).
(Time in hours.)

a similar rate in increase with time, while concentration 6 resulted in the greatest increase with time.

Figures 4.7 and 4.8 show the results of bromodichloromethane (CHCl_2Br) formation in phase A as a function of time and at six chlorine concentrations, for pH 7 and 9, respectively.

The CHCl_2Br concentration followed the general form of the breakpoint curve, at any given reaction time the concentration increased from concentrations 1 to 3 and then decreased at concentration 4. At chlorine concentrations 5 and 6 the concentration of CHCl_2Br increased as compared to those before the breakpoint.

Figures 4.9 and 4.10 show the results of (chlorodibromomethane (CHClBr_2) formation in phase A as a function of time, and chlorine concentration, at pH 7 and 9, respectively.

Figures 4.11 and 4.12 show the results of bromoform (CHBr_3) formation in phase A as a function of time, and at six chlorine concentrations, for pH 7 and 9, respectively. The concentration of CHBr_3 was small in phase A, no bromide was added to the groundwater sample.

In general, and as expected, longer reaction times, higher chlorine concentration and higher pH led to an increased concentration of THM's. The exception was chlorine concentration 4, which was at the break point where a minimum free residual of chlorine existed.

Examination of the data reveals that the concentration of chloroform is most significant among THM's followed by bromodichloromethane and chlorodibromomethane. The concentration of bromoform was minimal, as the groundwater was typical of a water with

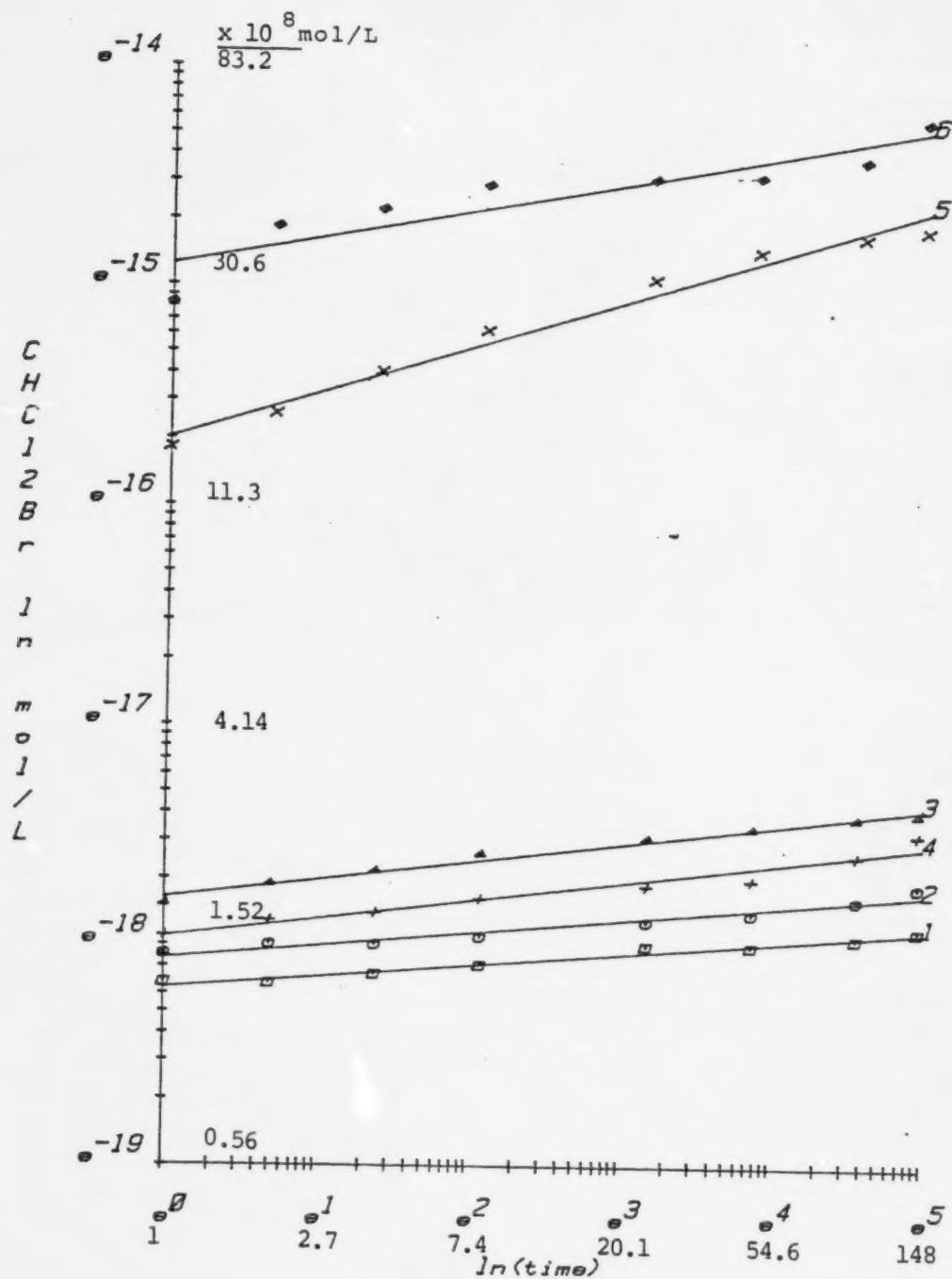


Fig. 4. 7. CHCl_2Br formation as a function of time at six chlorine concentrations (Phase A, No Bromide, pH 7).
(Time in hours.)

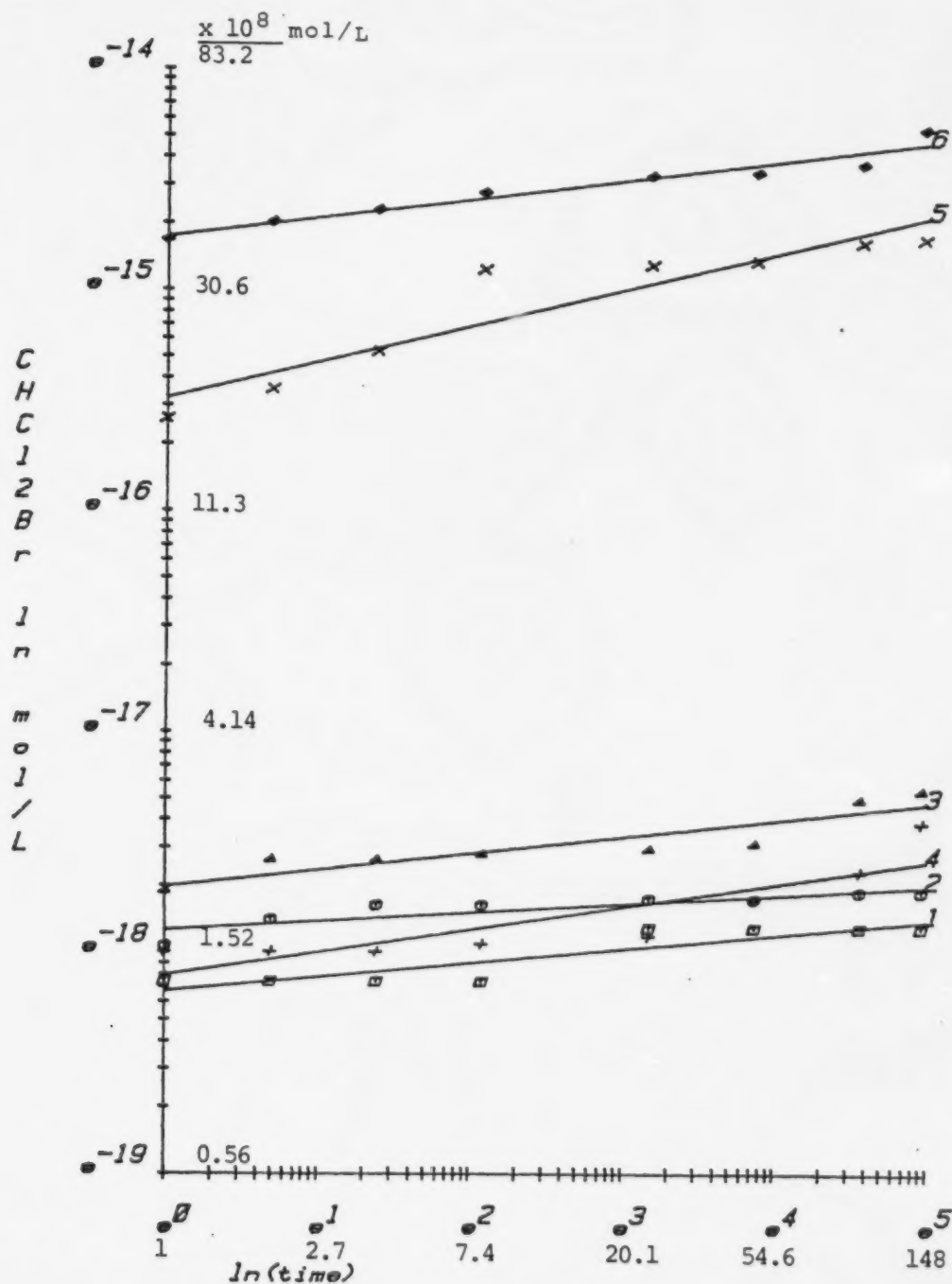


Fig. 4.8. CHCl_2Br formation as a function of time at six chlorine concentrations (Phase A, No Bromide, pH 9).
(Time in hours.)

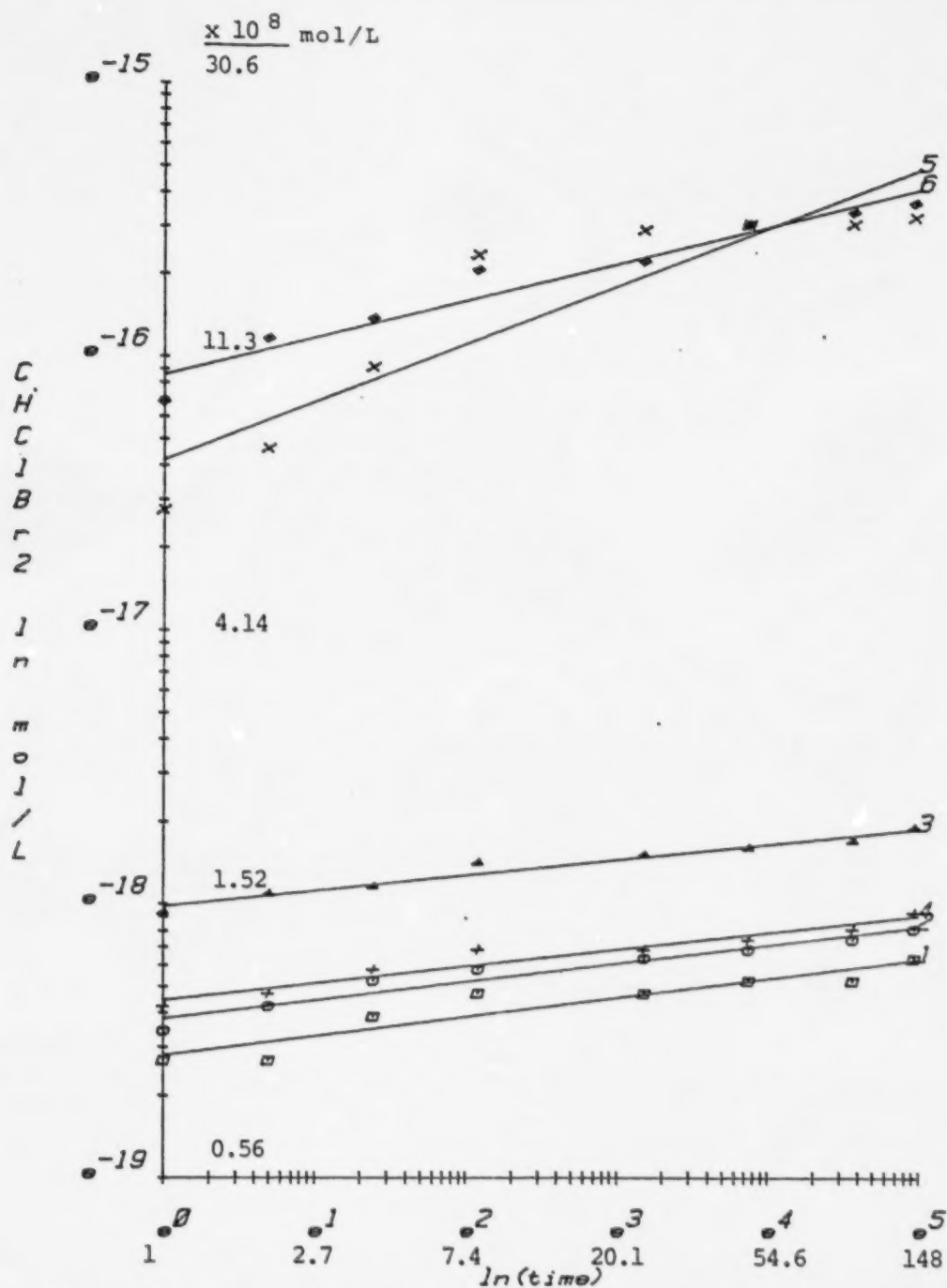


Fig. 4. 9. CHClBr_2 formation as a function of time at six chlorine concentrations (Phase A, No Bromide, pH 7).

(Time in hours.)

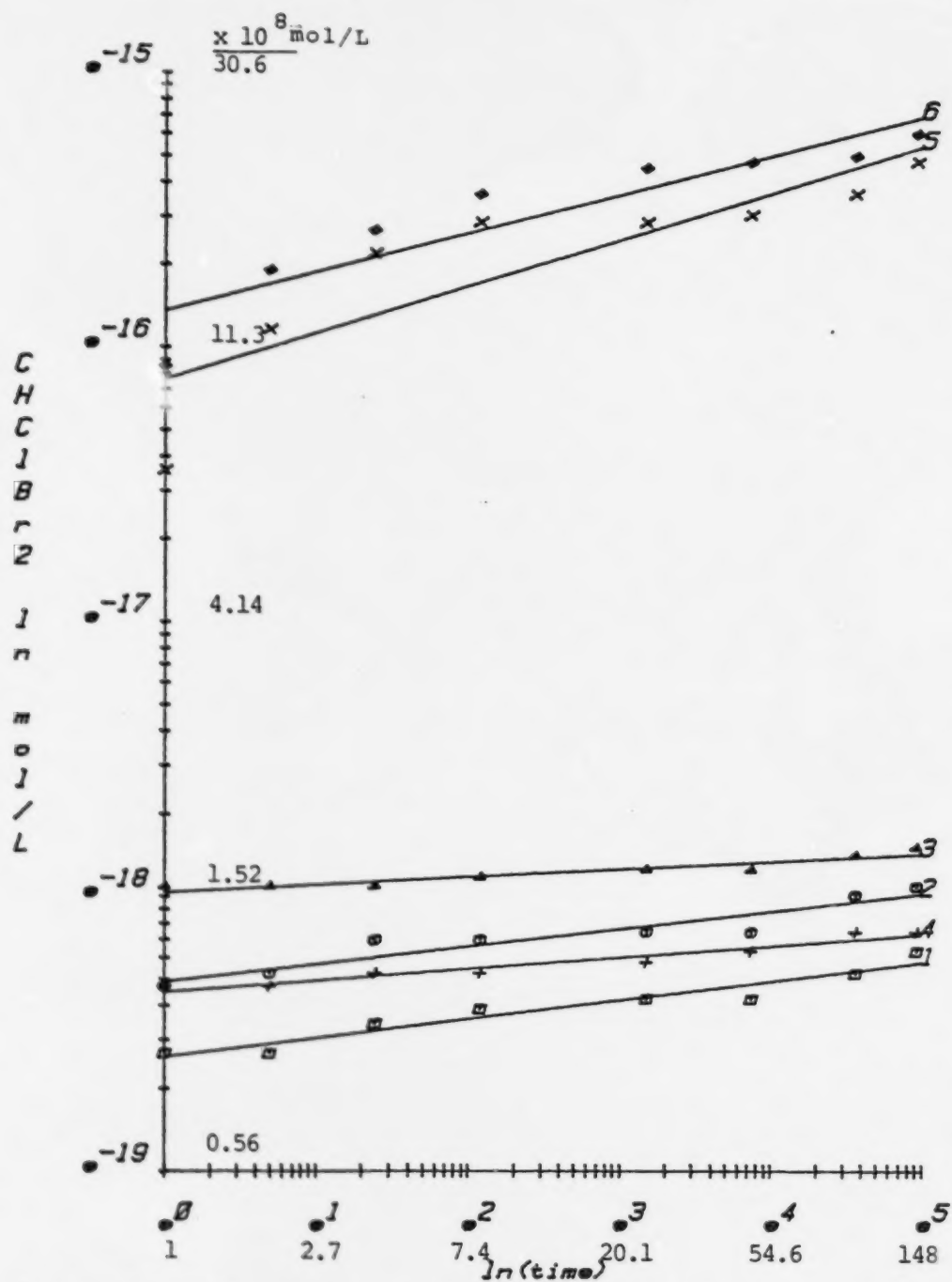


Fig. 4.10. CHClBr_2 formation as a function of time at six chlorine concentrations (Phase A, No Bromide, pH 9).

(Time in hours.)

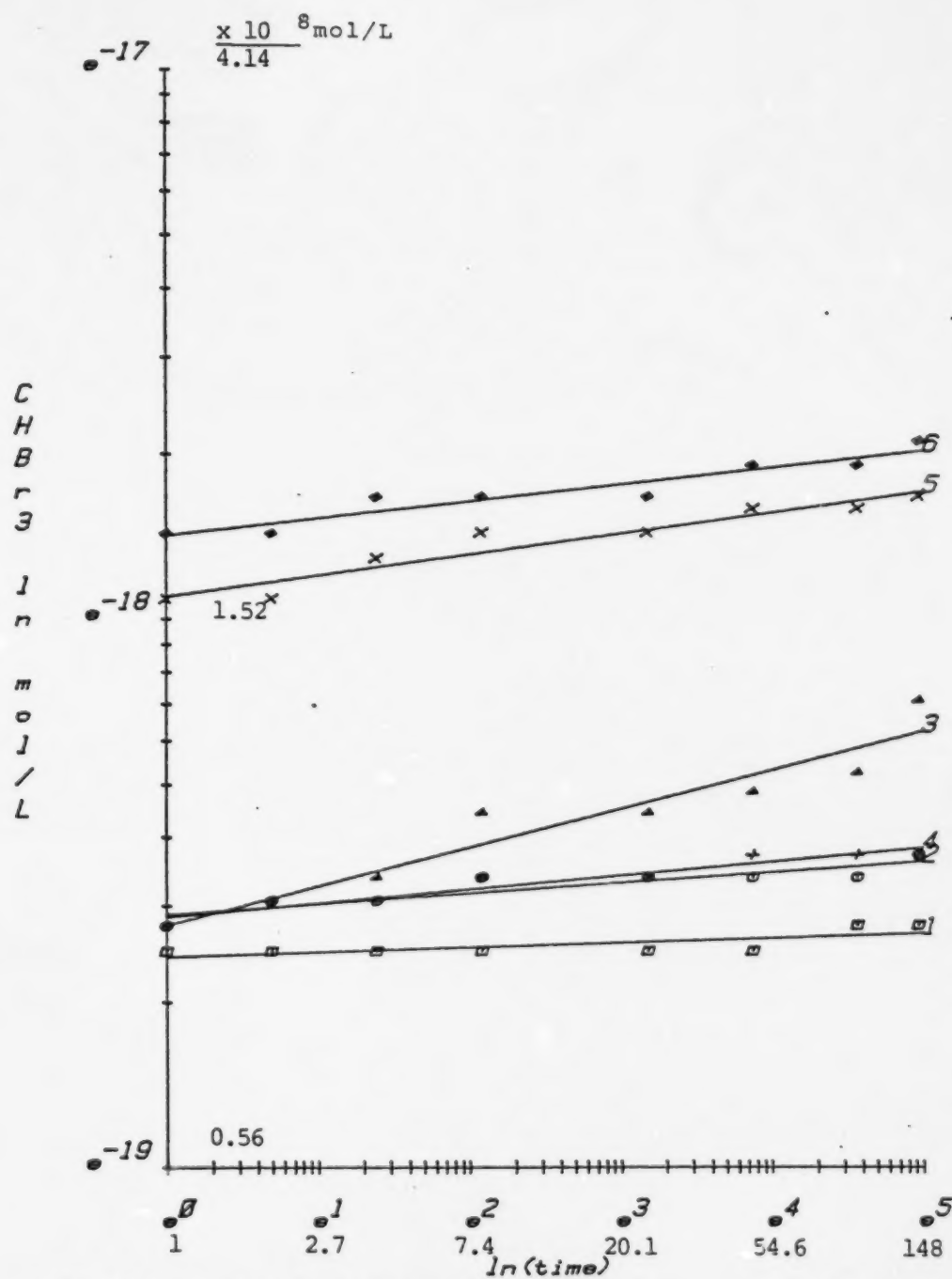


Fig. 4.11. CHBr_3 formation as a function of time at six chlorine concentrations (Phase A, No Bromide, pH 7).

(Time in hours.)

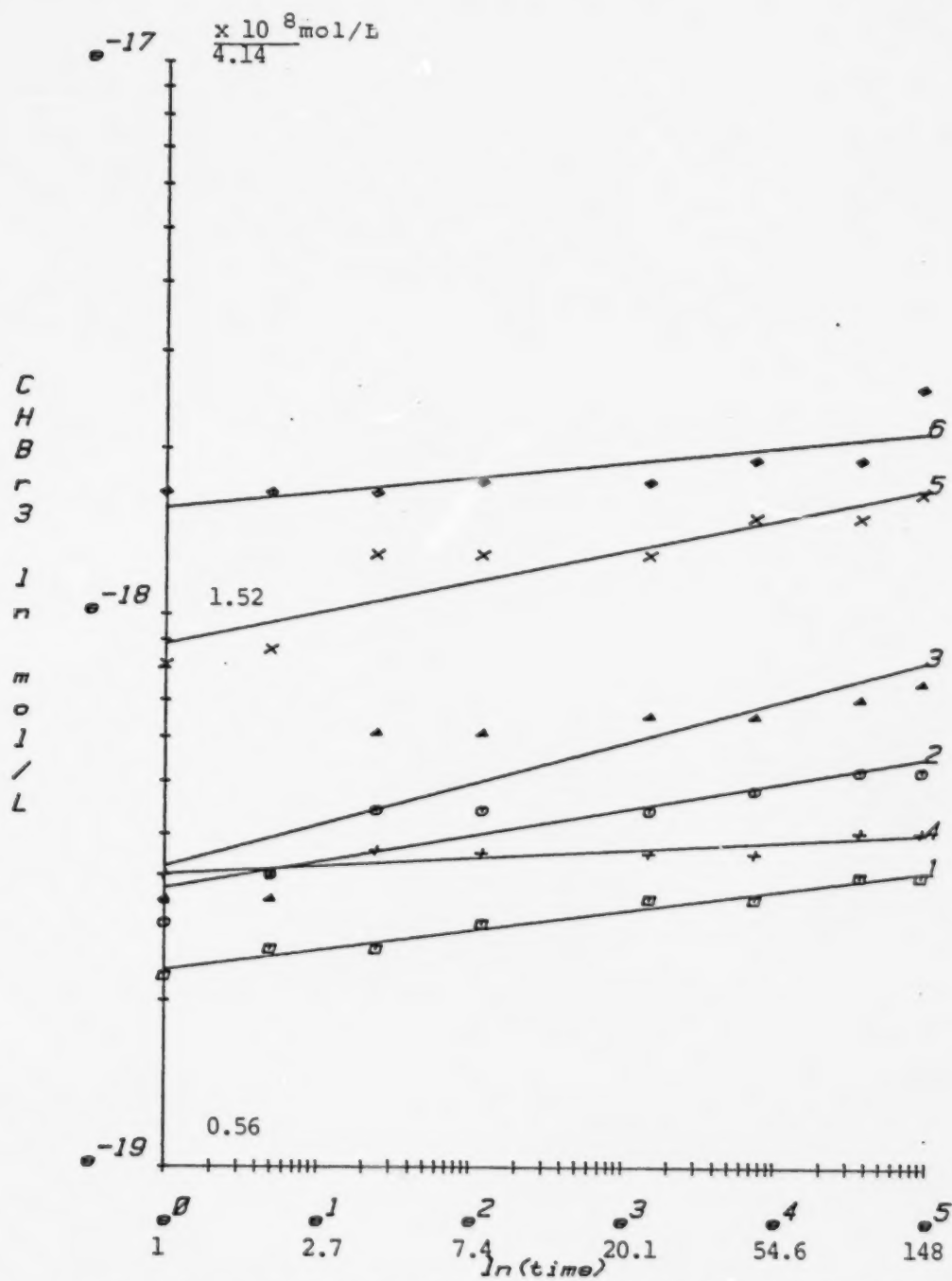


Fig. 4.12. CHBr_3 formation as a function of time at six chlorine concentrations (Phase A, No Bromide, pH 9).

(Time in hours.)

low Br^- . Consequently, the relative concentration in mol/L observed were:



Figures 4.13 and 4.14 show the result of the total trihalomethane (TTHM) formation in phase A as a function of time, and at six chlorine concentrations, for pH 7 and 9, respectively. TTHM concentration increased with time, higher chlorine concentration and higher pH. At chlorine concentration 4 which was located at the break point the concentration of TTHM decreased relative to that at chlorine concentration 3.

Figures 4.15 and 4.16 show the results of total organic Br in phase A as a function of time, and at six chlorine concentrations, for pH 7 and 9, respectively. The concentration of total organic Br was small in phase A because no bromide was added to the groundwater sample. The concentration of total organic Br at 144 hours reaction time was below 110×10^{-9} mol/L at chlorine concentrations 1, 2, 3 and 4 at both pH 7 and 9. At chlorine concentration 5 at 144 hours reaction time it was 826×10^{-9} mol/L at pH 7 and 881×10^{-9} mol/L at pH 9. At chlorine concentration 6 total organic Br was 1100×10^{-9} mol/L at 144 hours reaction time at pH 7 and 1190×10^{-9} mol/L at pH 9.

Figures 4.17 and 4.18 show the results of total organic Cl in phase A as a function of time, and at six chlorine concentrations, at pH 7 and 9, respectively. The concentration at 144 hours reaction time was below 633×10^{-9} mol/L at chlorine concentrations 1, 2, 3 and 4 at both pH 7 and 9. At chlorine concentration 5 the total organic Cl was 3370×10^{-9} mol/L at pH 7 and 3400×10^{-9} mol/L

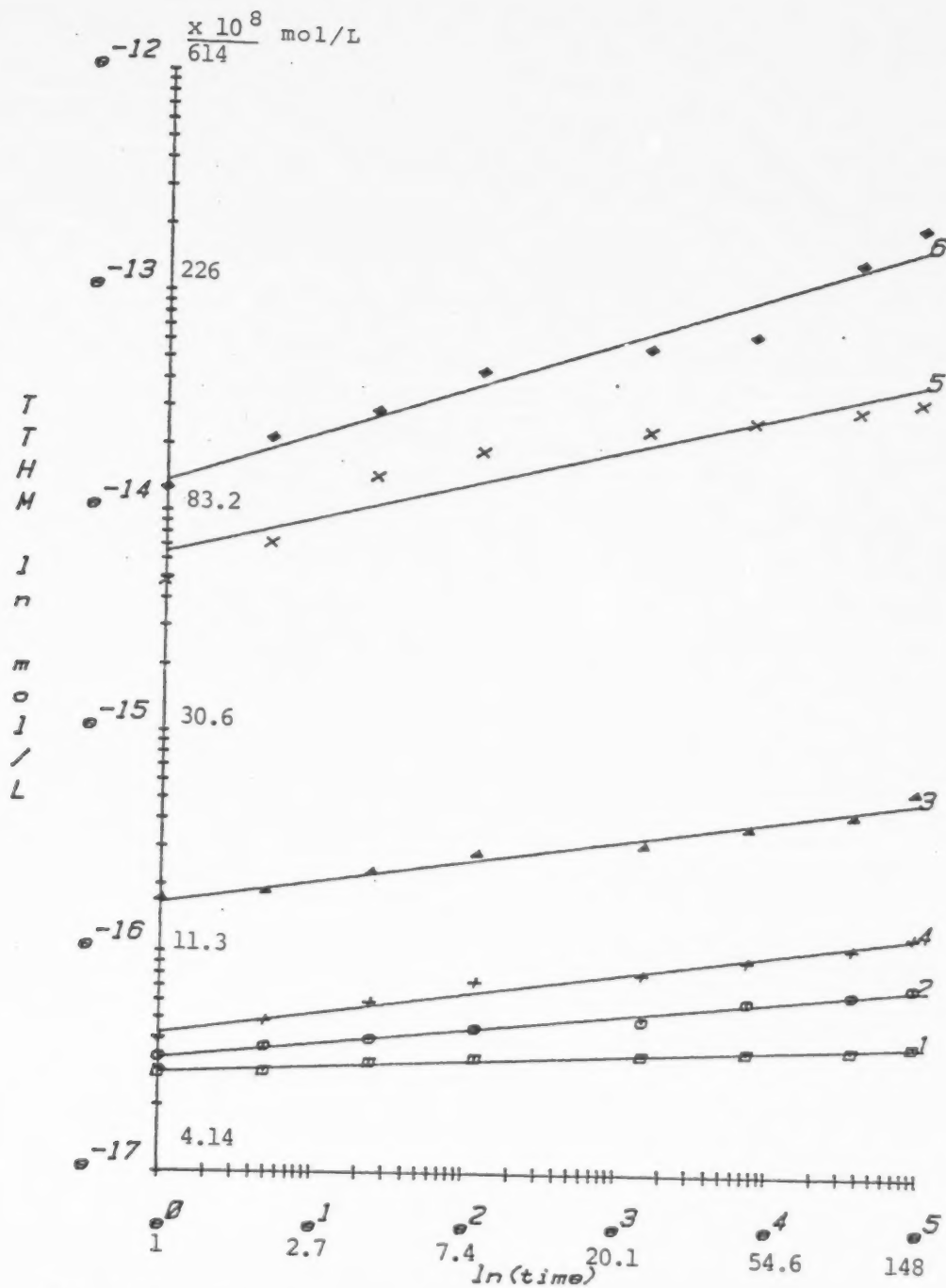


Fig. 4.13. THM formation as a function of time at six chlorine concentrations (Phase A, No Bromide, pH 7).
(Time in hours.)

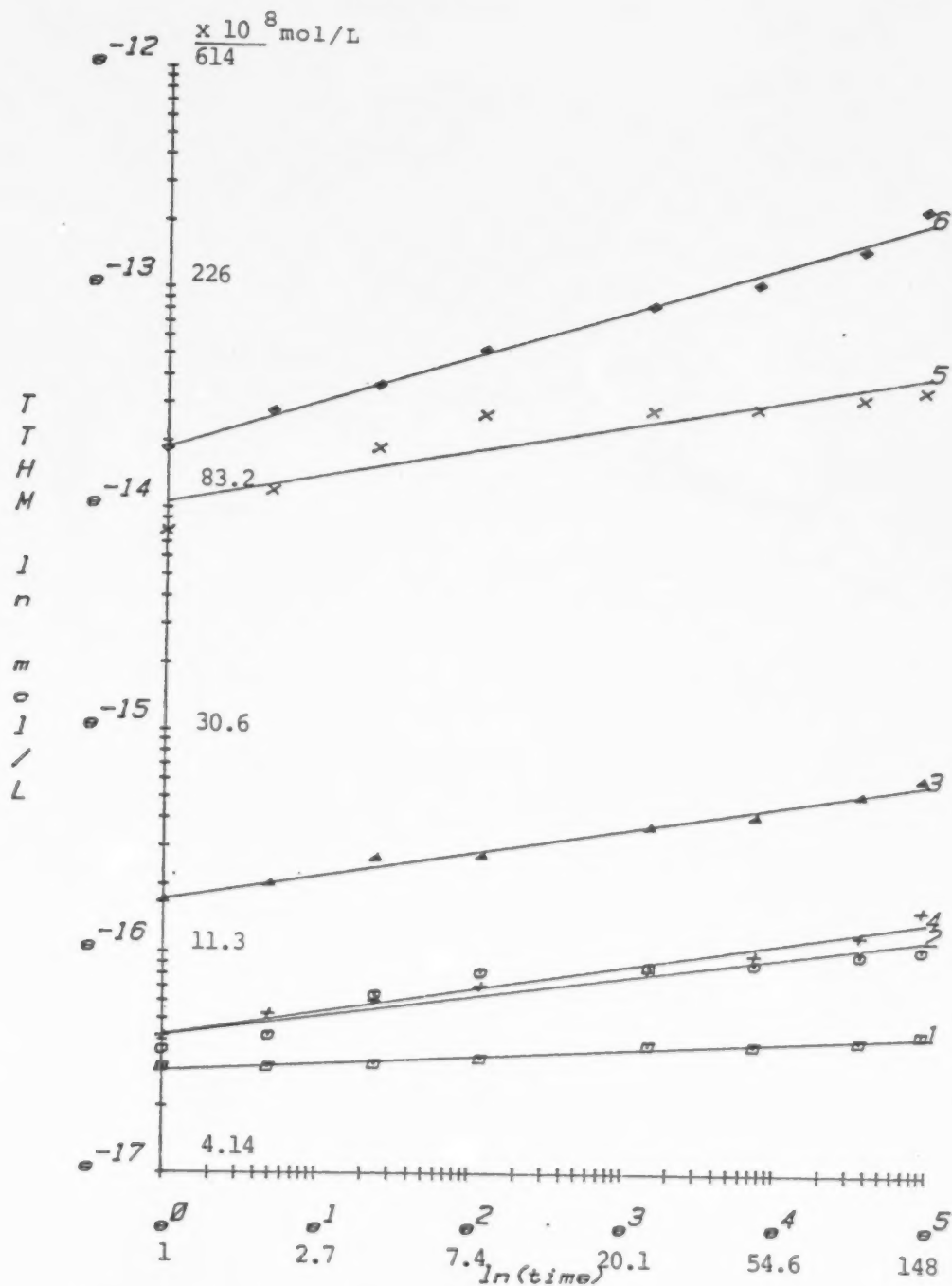


Fig. 4.14. TTHM formation as a function of time at six chlorine concentrations (Phase A, No Bromide, pH 9).
(Time in hours.)

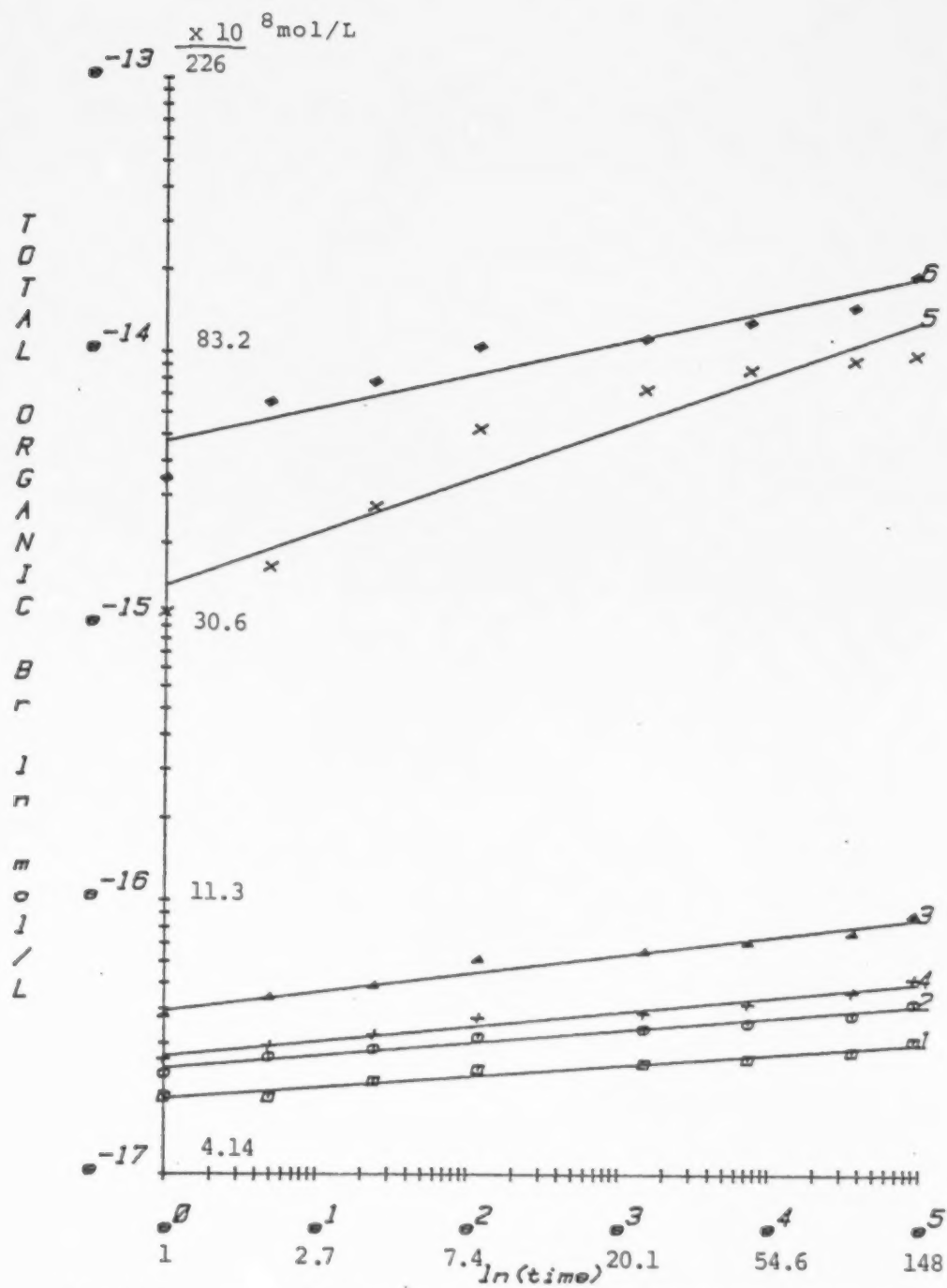


Fig. 4.15. Total Organic Br formation as a function of time at six chlorine concentrations (Phase A, No Bromide, pH 7).
(Time in hours.)

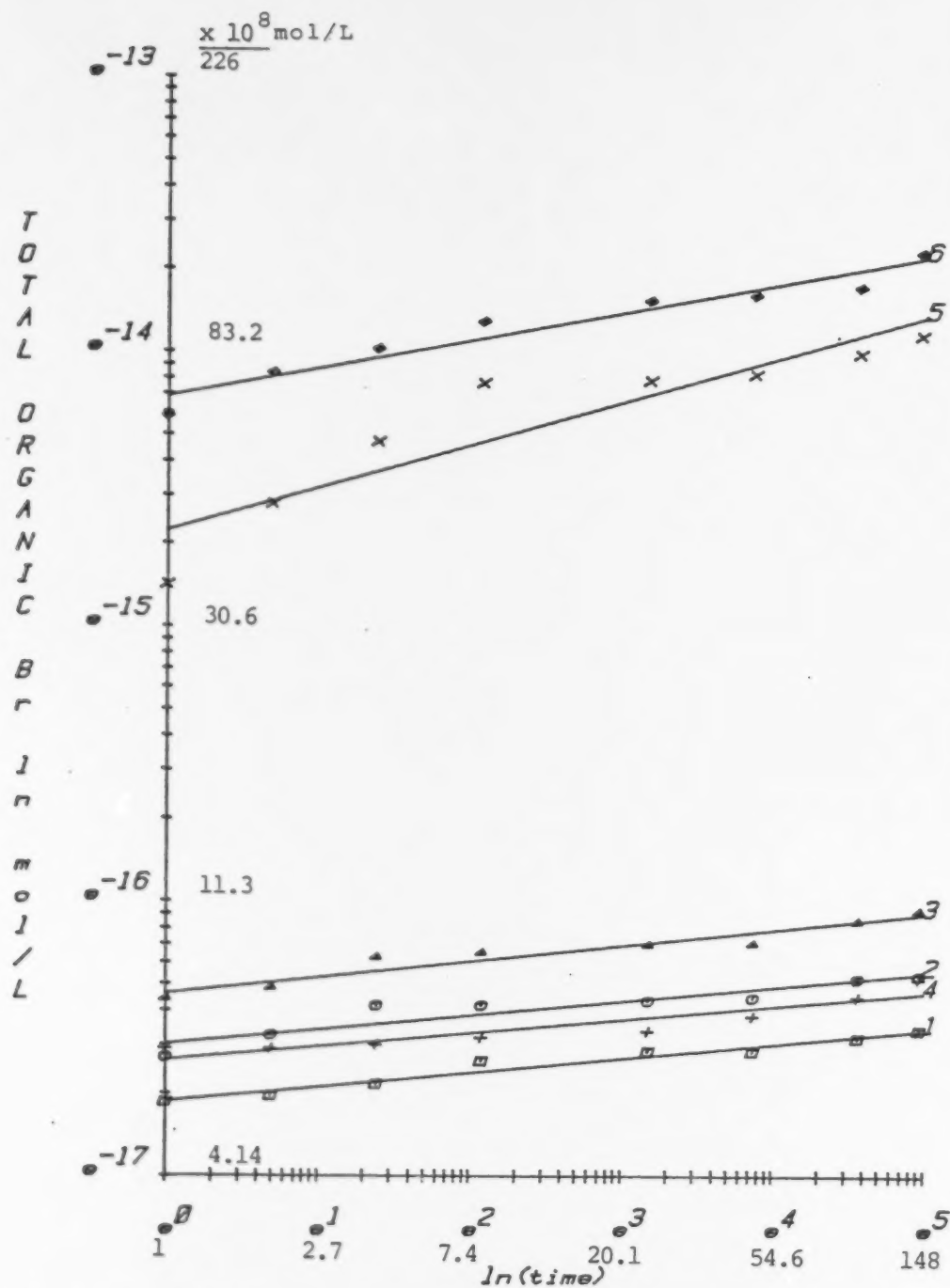


Fig. 4.16. Total organic Br formation as a function of time at six chlorine concentrations (Phase A, No Bromide, pH 9).
(Time in hours.)

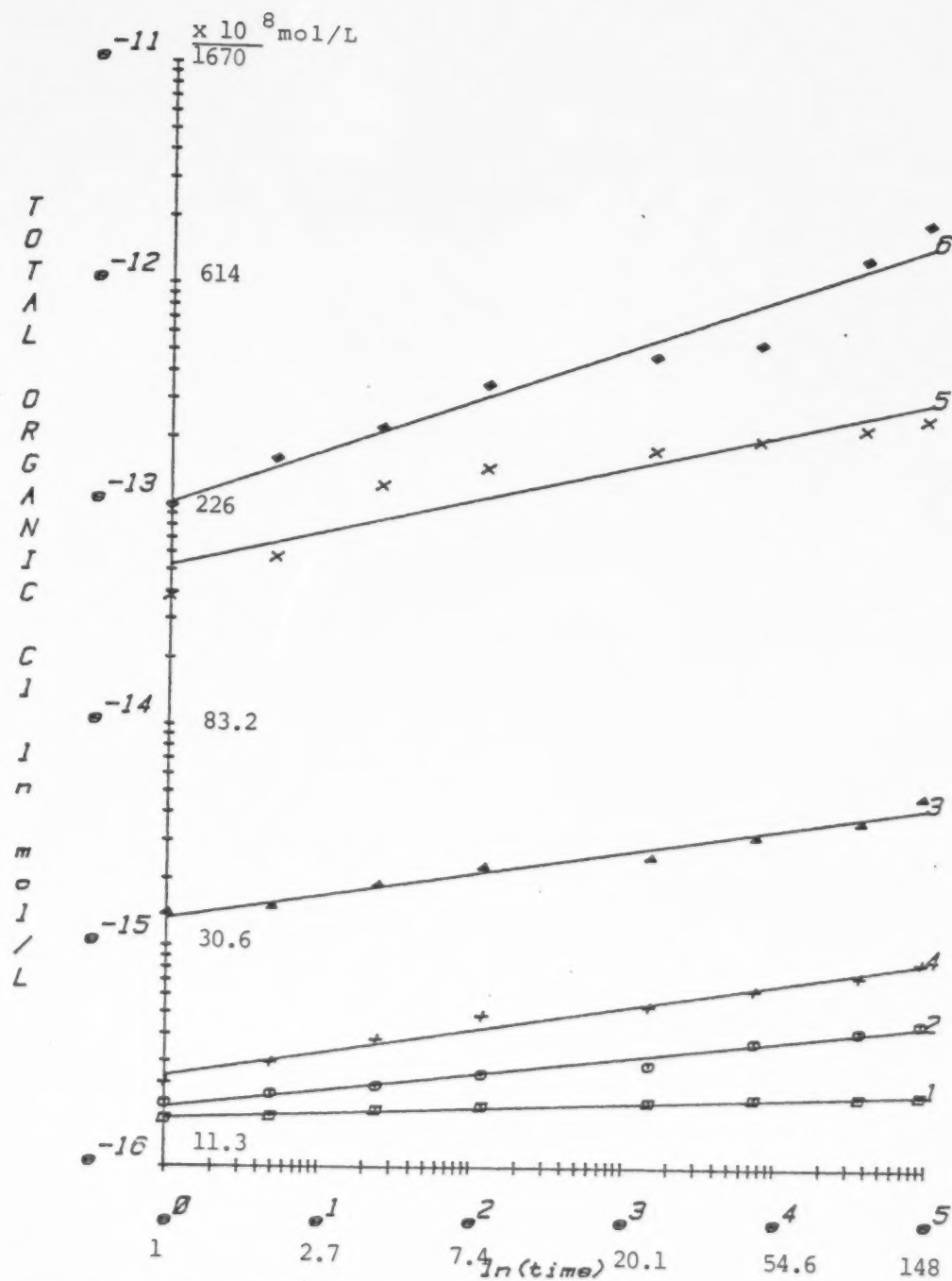


Fig. 4.17. Total organic Cl formation as a function of time at six chlorine concentrations (Phase A, No Bromide, pH 7).

(Time in hours.)

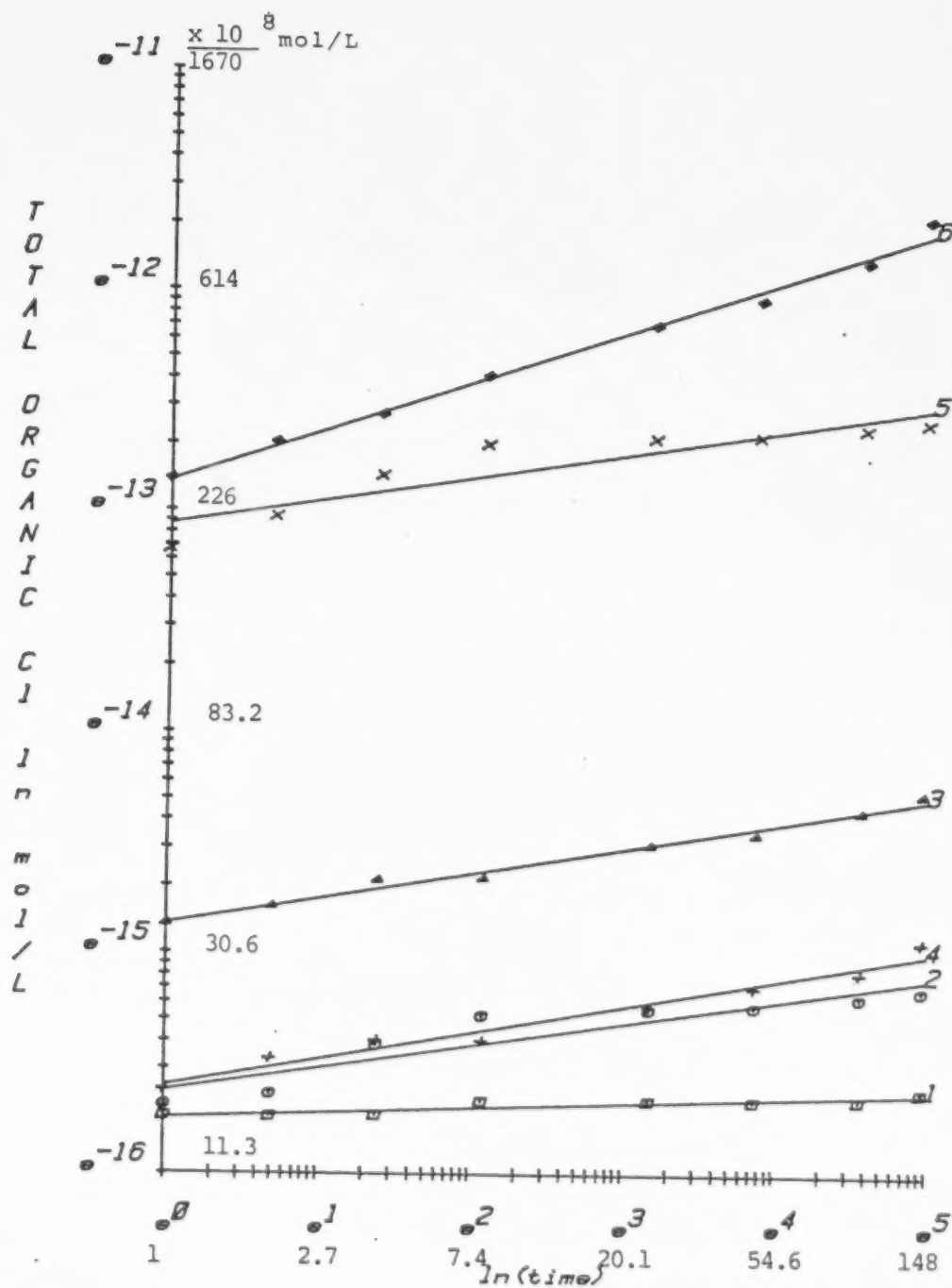


Fig. 4.18. Total organic Cl formation as a function of time at six chlorine concentrations (Phase A, No Bromide, pH 9).
(Time in hours.)

at pH 9 after 144 hours reaction time. At chlorine concentration 6 the concentration was 8150×10^{-9} mol/L at pH 7 and 8520×10^{-9} mol/L at pH 9 after 144 hours reaction time.

The mole ratio of total organic Cl to Br fluctuated throughout the eight reaction times in experimental phase A. Table 4.13 presents the mole ratio of total organic Cl/Br throughout the eight reaction times in experimental phase A. No consistent pattern was developed in this ratio where no Br^- was added to the ground water.

In general, the incorporated percentage of Cl increased at higher chlorine concentrations and pH with the exception of chlorine concentration 4 which was at the break point. Table 4.14 presents mole percent Cl incorporated at minimum (1) and maximum (144) hours reaction times in experimental phase A. Even at pH 9 and chlorine concentration 6, only 1.68% of the Cl added was accounted for in the trihalomethanes.

Experimental Phase B: The condition designated for this phase was the addition of 1×10^{-6} mol/L Br^- to groundwater prior to chlorination. The formation and distribution of THM's was investigated as a function of time, pH and chlorine concentration. The chlorine concentrations used in phase B are given in Table 4.5 and shown in Figure 4.2.

The concentration of CHCl_3 as a function of time and at six chlorine concentrations is shown in Figure 4.19 and 4.20, for pH 7 and 9, respectively.

The concentration of chloroform was shown in a general way to follow the shape of the breakpoint curve in experimental phase B. The

TABLE 4.13

THE MOLE RATIO OF ORGANIC Cl/Br THROUGHTOUT
EIGHT REACTION TIMES (HOURS) IN EXPERIMENTAL PHASE A.

Chlorine Concentration Number	pH	Range
1	7	2.34 - 2.59
	9	2.32 - 2.69
2	7	2.47 - 2.83
	9	2.34 - 3.04
3	7	4.62 - 5.70
	9	4.41 - 5.81
4	7	2.62 - 3.39
	9	2.51 - 3.81
5	7	3.90 - 5.19
	9	3.86 - 5.34
6	7	4.02 - 7.41
	9	3.97 - 7.16

TABLE 4.14

THE MOLE PERCENT Cl INCORPORATED AT MINIMUM (1) AND
MAXIMUM (144) HOURS REACTION TIME IN EXPERIMENTAL PHASE A.

Chlorine Concentration Number	pH	Reaction Time (hours)	
		1	144
1	7	0.496	0.560
	9	0.518	0.585
2	7	0.133	0.193
	9	0.136	0.230
3	7	0.210	0.361
	9	0.206	0.375
4	7	0.073	0.127
	9	0.073	0.144
5	7	0.441	0.997
	9	0.562	1.01
6	7	0.441	1.60
	9	0.514	1.68

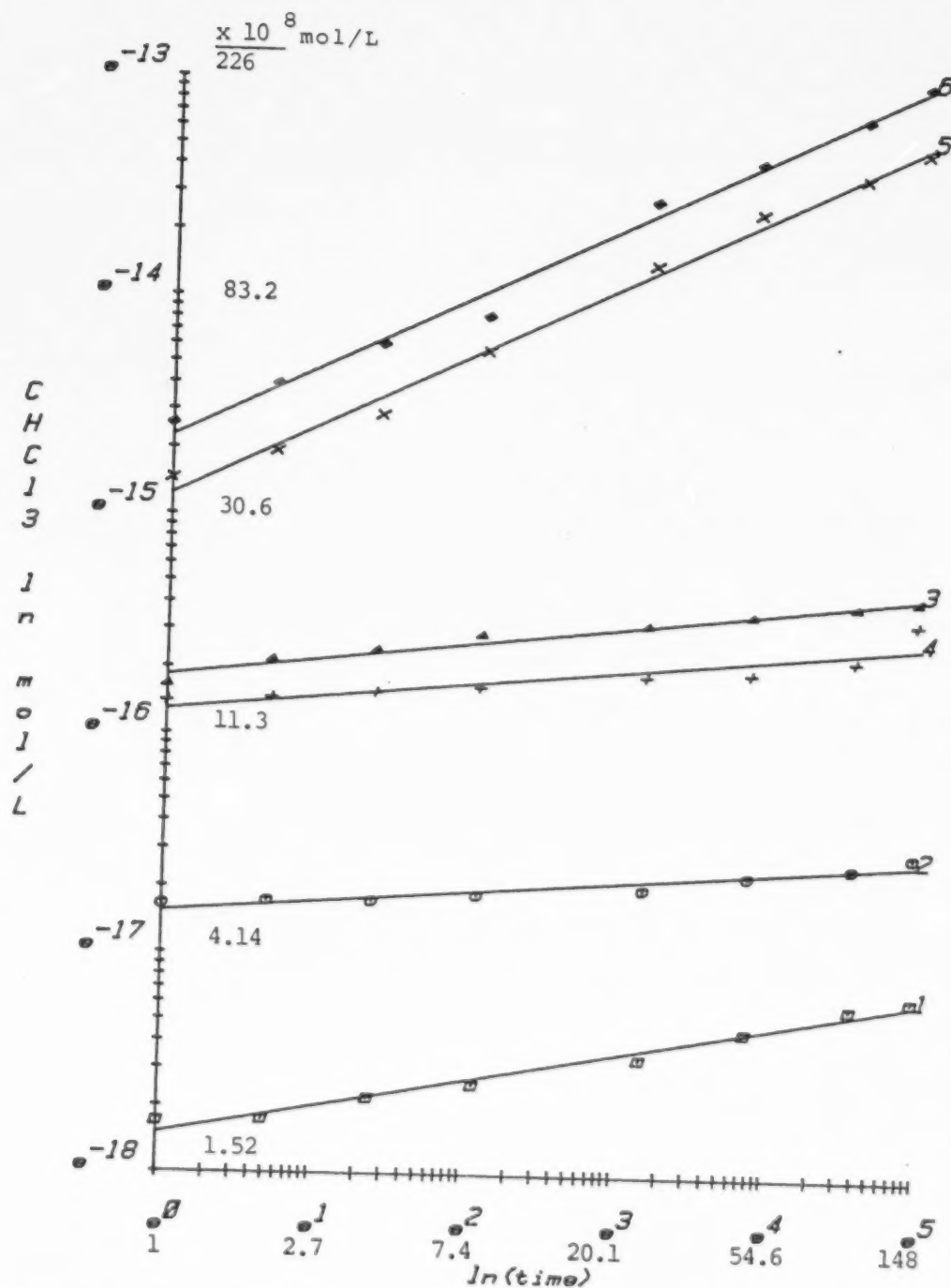


Fig. 4.19. CHCl_3 formation as a function of time at six chlorine concentrations (Phase B, 1×10^{-6} mol/L Bromide, pH 7). (Time in hours.)

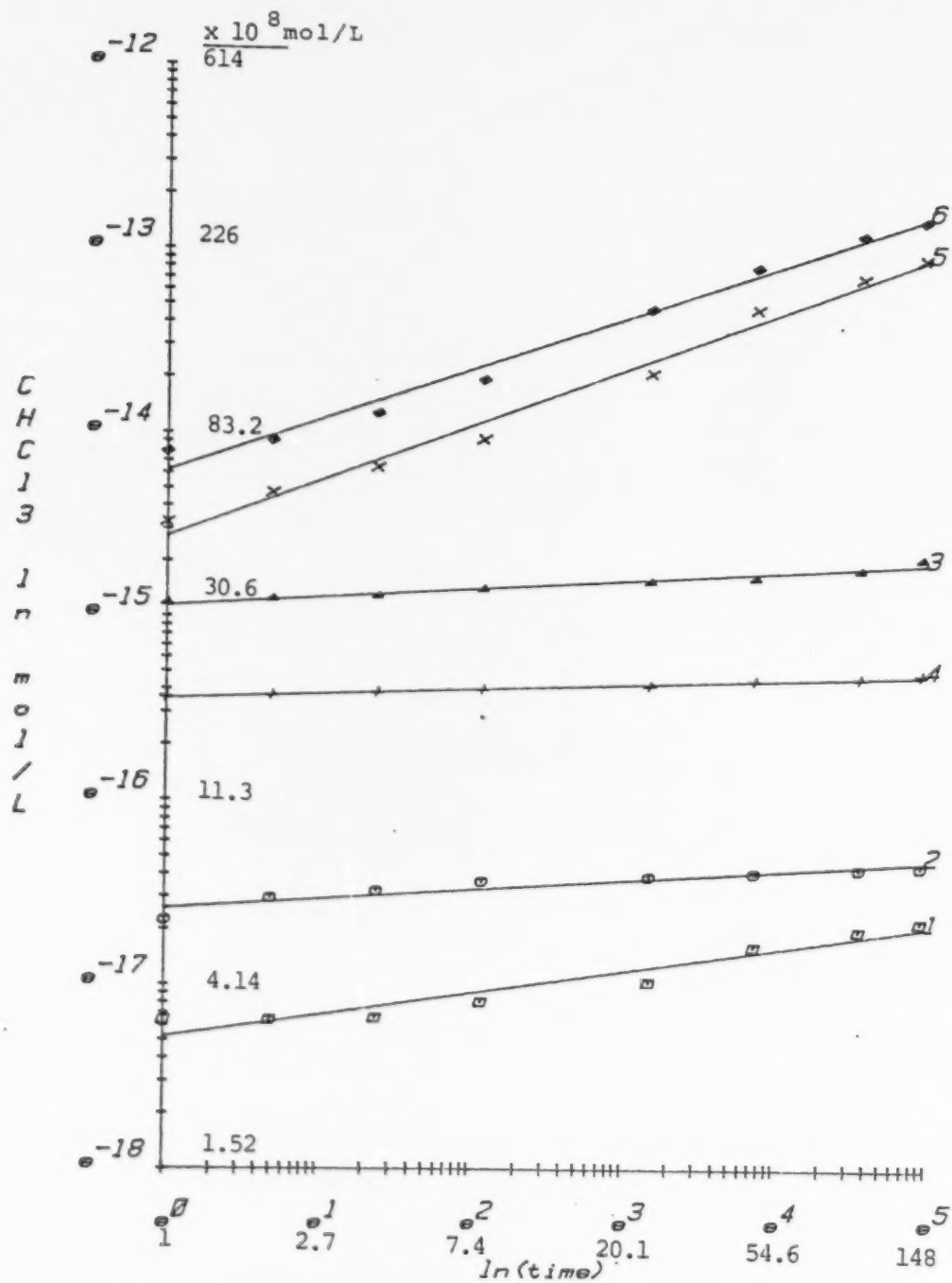


Fig. 4.20. CHCl_3 formation as a function of time at six chlorine concentrations (Phase B, $1 \times 10^{-6} \text{ mol/L}$ Bromide, pH 9). (Time in hours.)

chloroform concentration at all chlorine concentrations increased from chlorine concentration one to three, decreased at chlorine concentration 4 and increased at 5 and 6. At pH 9 the concentration CHCl_3 , was higher than the corresponding pH 7 value, the difference being most significant after the break point.

The slopes of the curves (rate of reaction) in Figure 4.19 and 4.20 were similar at both pH levels. At chlorine concentration 1 the CHCl_3 increased in concentration with time at both pH levels, the pH 9 rate of increase was higher than pH 7. At chlorine concentration 2 the slope of the curve at both pH levels was approximately level, i.e. no increase in CHCl_3 concentration with time. Chlorine concentration 3 and 4 showed a similar rate of increase with time. Chlorine concentration 5 and 6 showed the greatest increase with reaction time.

Figures 4.21 and 4.22 show the results of CHCl_2Br formation in phase B as a function of time, and at six chlorine concentrations, for pH 7 and 9, respectively.

The CHCl_2Br concentration followed the general form of the breakpoint curve, at any given reaction time the concentration increased from concentration 1 to 3 and then decreased at concentration 4. At chlorine concentrations 5 and 6 the concentration of CHCl_2Br increased as compared to those before the breakpoint.

Figures 4.23 and 4.24 show the results of CHClBr_2 formation in phase B as a function of time, and at six chlorine concentrations, for pH 7 and 9, respectively. These results followed a pattern similar to those of CHCl_2Br , above.

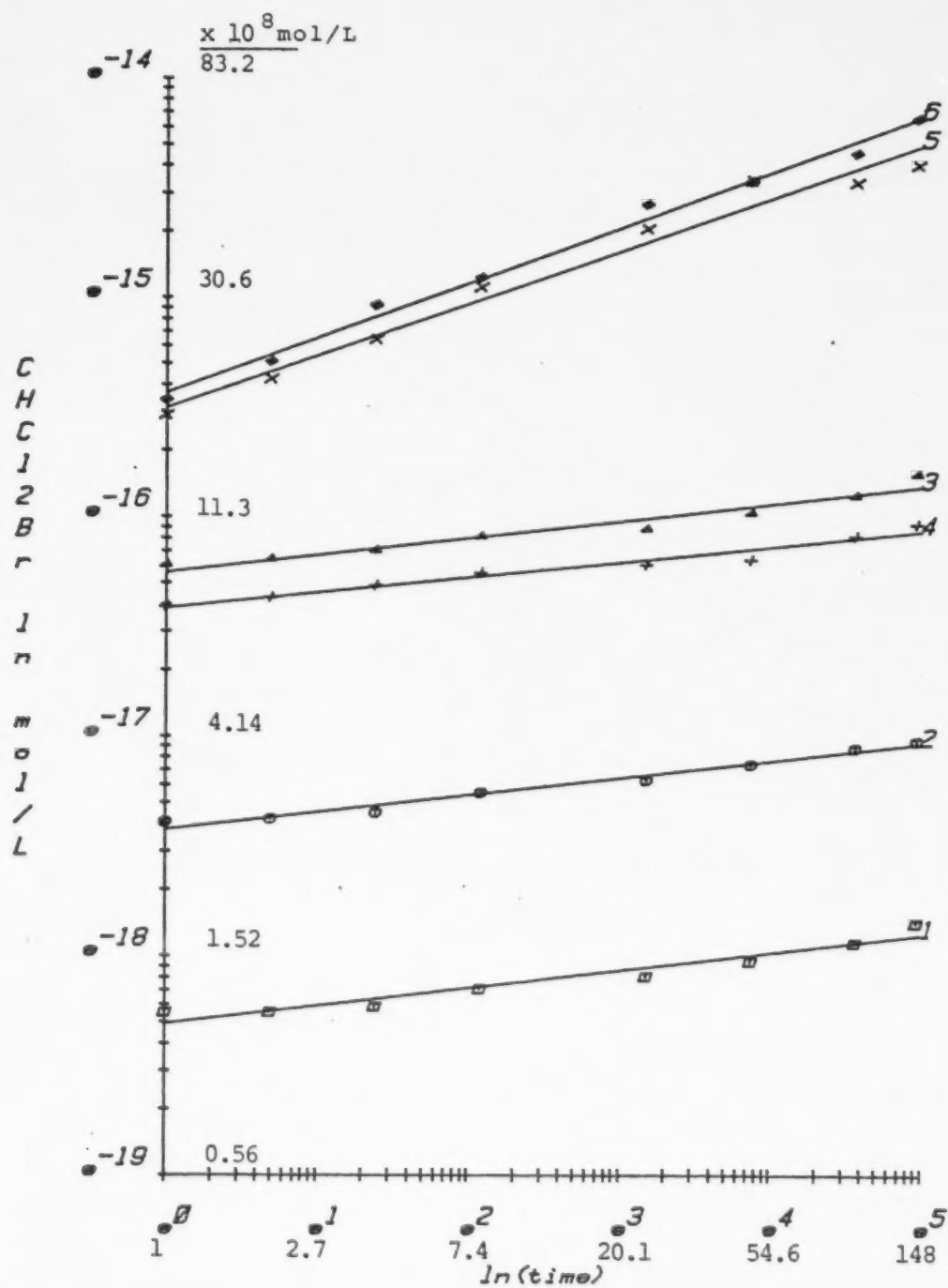


Fig. 4.21. CHCl_2Br formation as a function of time at six chlorine concentrations (Phase B, 1×10^{-6} mol/L Bromide, pH 7). (Time in hours.)

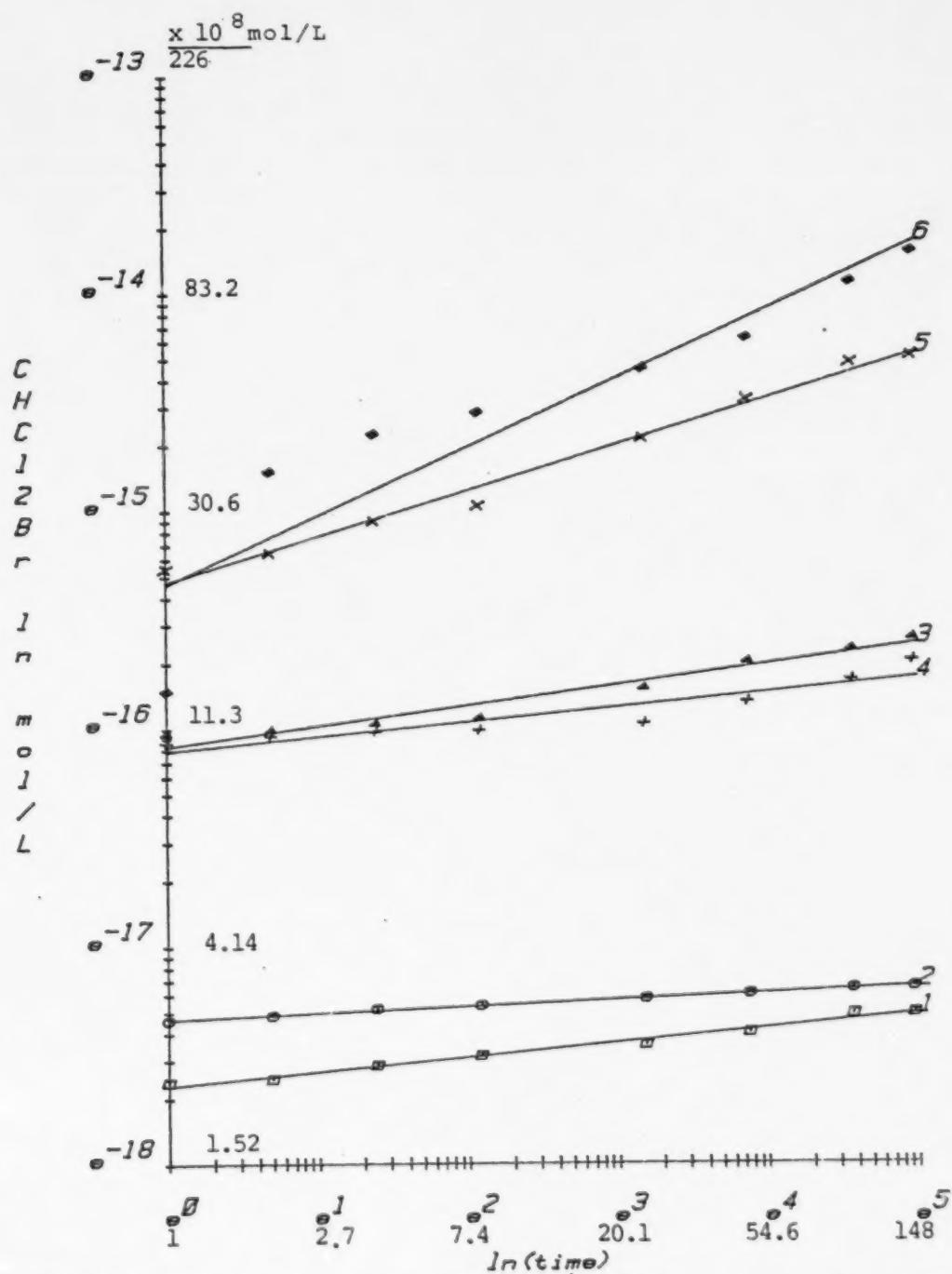


Fig. 4.22. CHCl_2Br formation as a function of time at six chlorine concentrations (Phase B, $1 \times 10^{-6} \text{ mol/L}$ Bromide, pH 9). (Time in hours.)

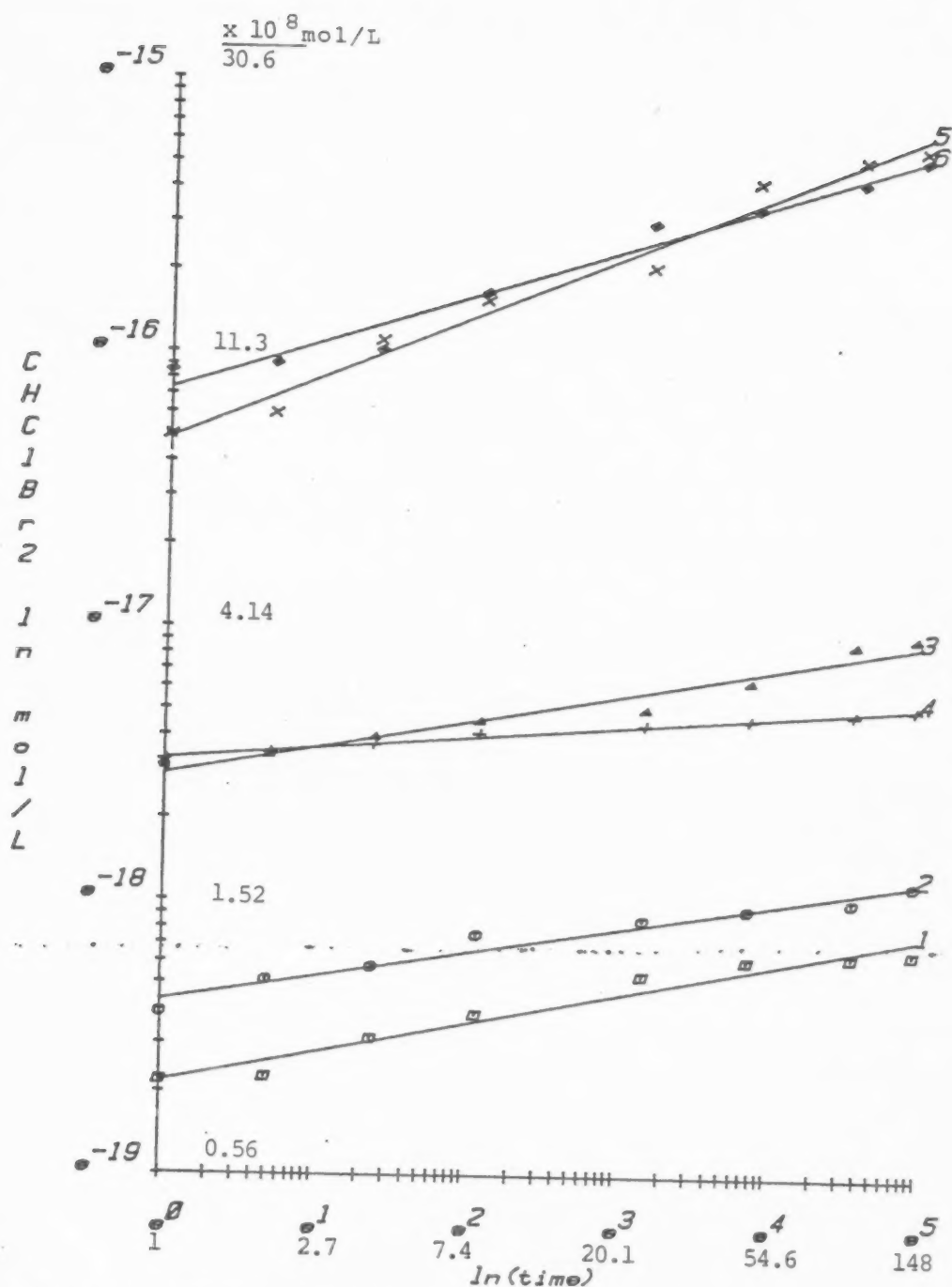


Fig. 4.23. CHClBr_2 formation as a function of time at six chlorine concentrations (Phase B, 1×10^{-6} mol/L Bromide, pH 7). (Time in hours.)

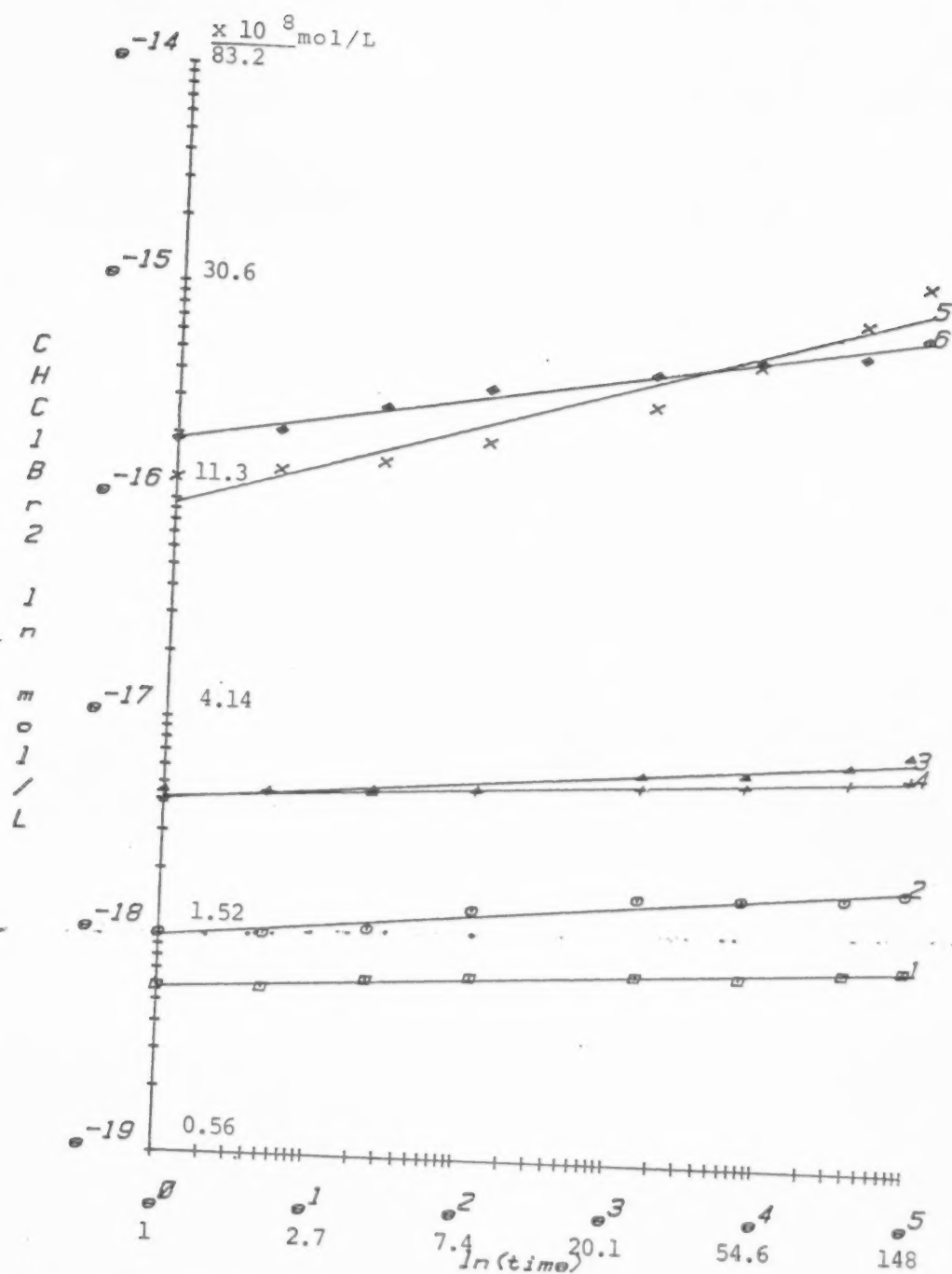


Fig. 4.24. CHClBr₂ formation as a function of time at six chlorine concentrations (Phase B, 1×10^{-6} mol/L Bromide, pH 9). (Time in hours.)

Figures 4.25 and 4.26 show the result of CHBr_3 formation in phase B as a function of time, and at six chlorine concentrations, for pH 7 and 9 respectively. The concentration of bromoform (CHBr_3) was higher in phase B than phase A due to the addition of 1×10^{-6} mol/L of bromide in groundwater.

Examination of data reveals that in spite of addition 1×10^{-6} mol/L Br^- to groundwater the concentration of chloroform was the highest among the THM's, followed by bromodichloromethane and dibromochloromethane. The concentration of bromoform was minimal, however, it was slightly higher than phase A. The relative concentration in mol/L observed were:



Figures 4.27 and 4.28 show the results of TTHM formation in phase B as a function of time and chlorine concentrations for pH 7 and 9, respectively. TTHM concentration increased with time, higher chlorine concentration and higher pH except at chlorine, concentration 4, break point.

Figures 4.29 and 4.30 show the results of total organic Br in phase B as a function of time, and at six chlorine concentrations, for pH 7 and 9, respectively. The concentration of total organic Br was significantly higher than in phase A (which had no Br^- added to groundwater). The concentration of total organic Br at 144 hours reaction time was below 342×10^{-9} mol/L for all chlorine concentrations 1, 2, 3 and 4 at both pH 7 and 9. At chlorine concentration 5 after 144 hours reaction time it was 1750×10^{-9} mol/L and at pH 9, 1300×10^{-9} mol/L at pH 7. At chlorine

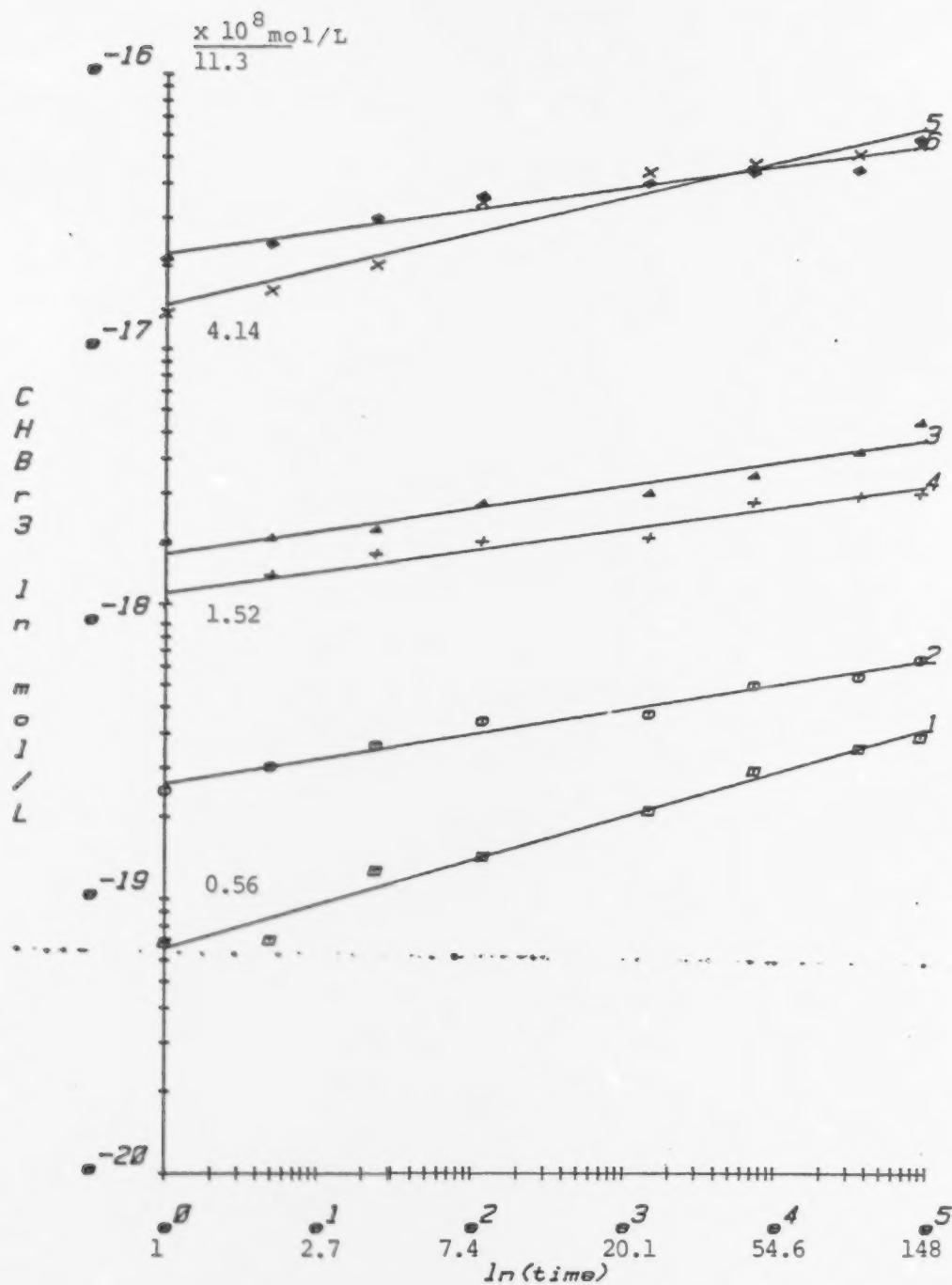


Fig. 4.25. CHBr_3 formation as a function of time at six chlorine concentrations (Phase B, $1 \times 10^{-6} \text{ mol/L}$ Bromide, pH 7). (Time in hours.)

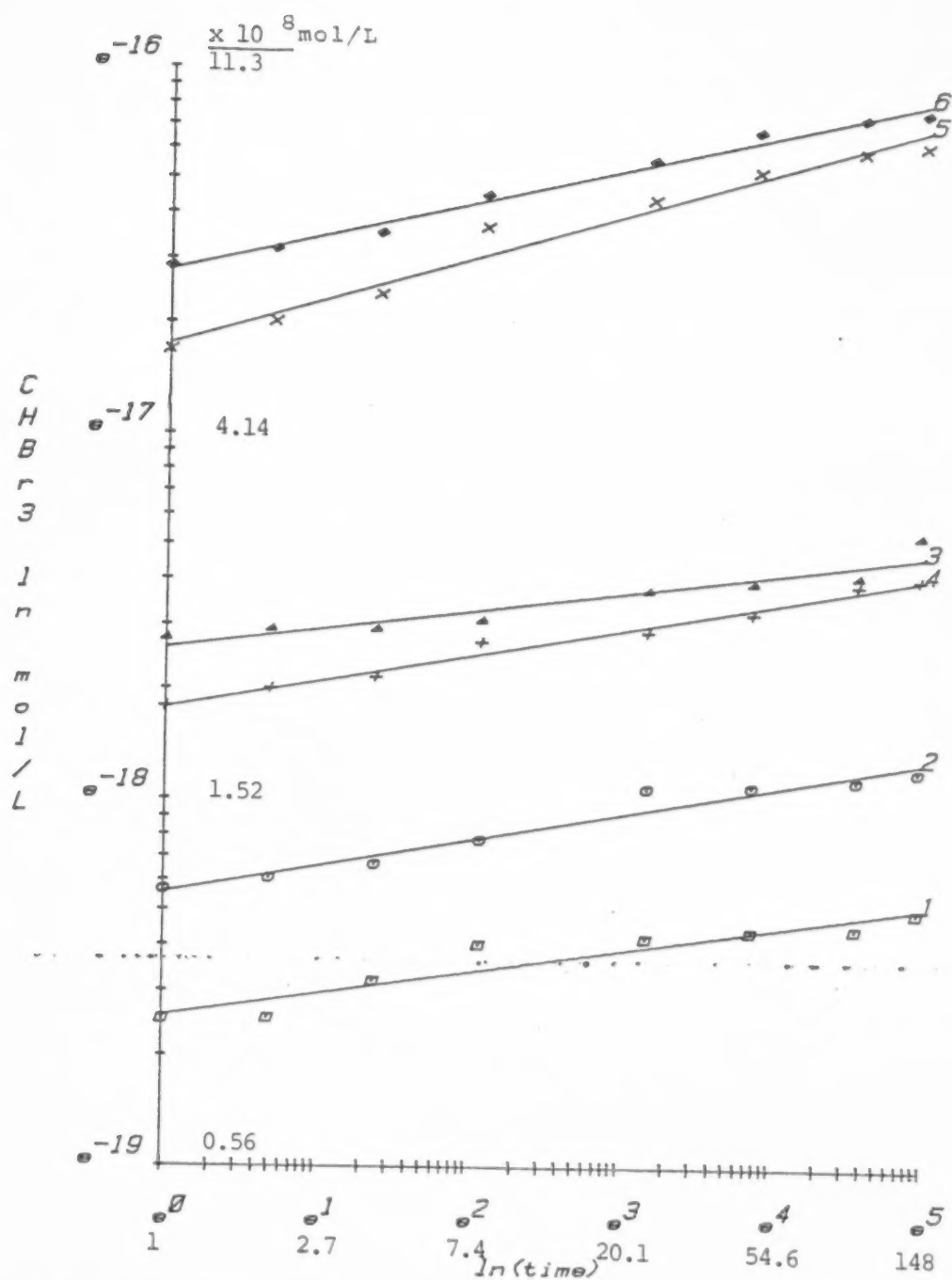


Fig. 4.26. CHBr_3 formation as a function of time at six chlorine concentrations (Phase B, 1×10^{-6} mol/L Bromide, pH 9). (Time in hours.)

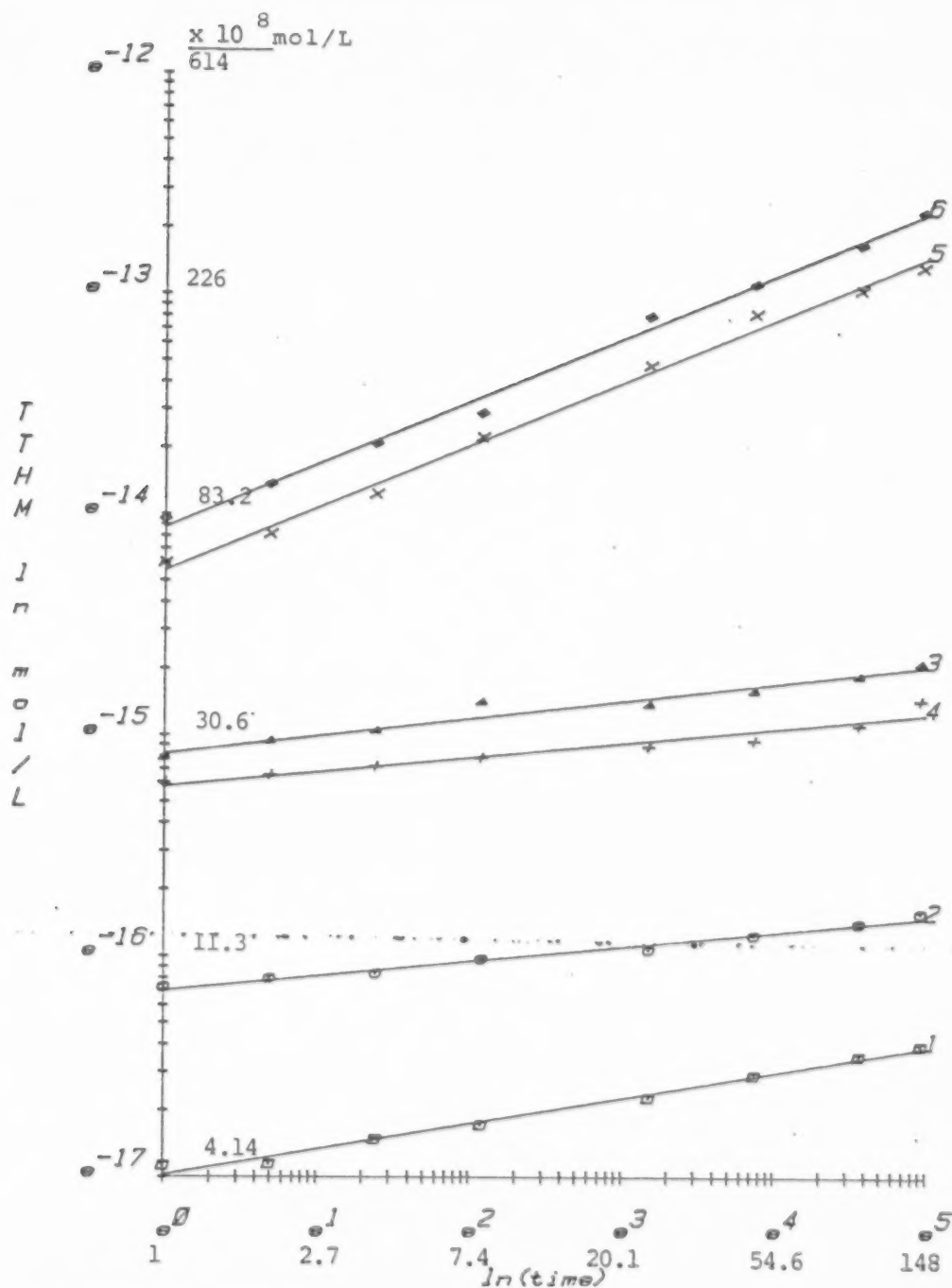


Fig. 4.27. TTHM formation as a function of time at six chlorine concentrations (Phase B, 1×10^{-6} mol/L Bromide, pH 7). (Time in hours.)

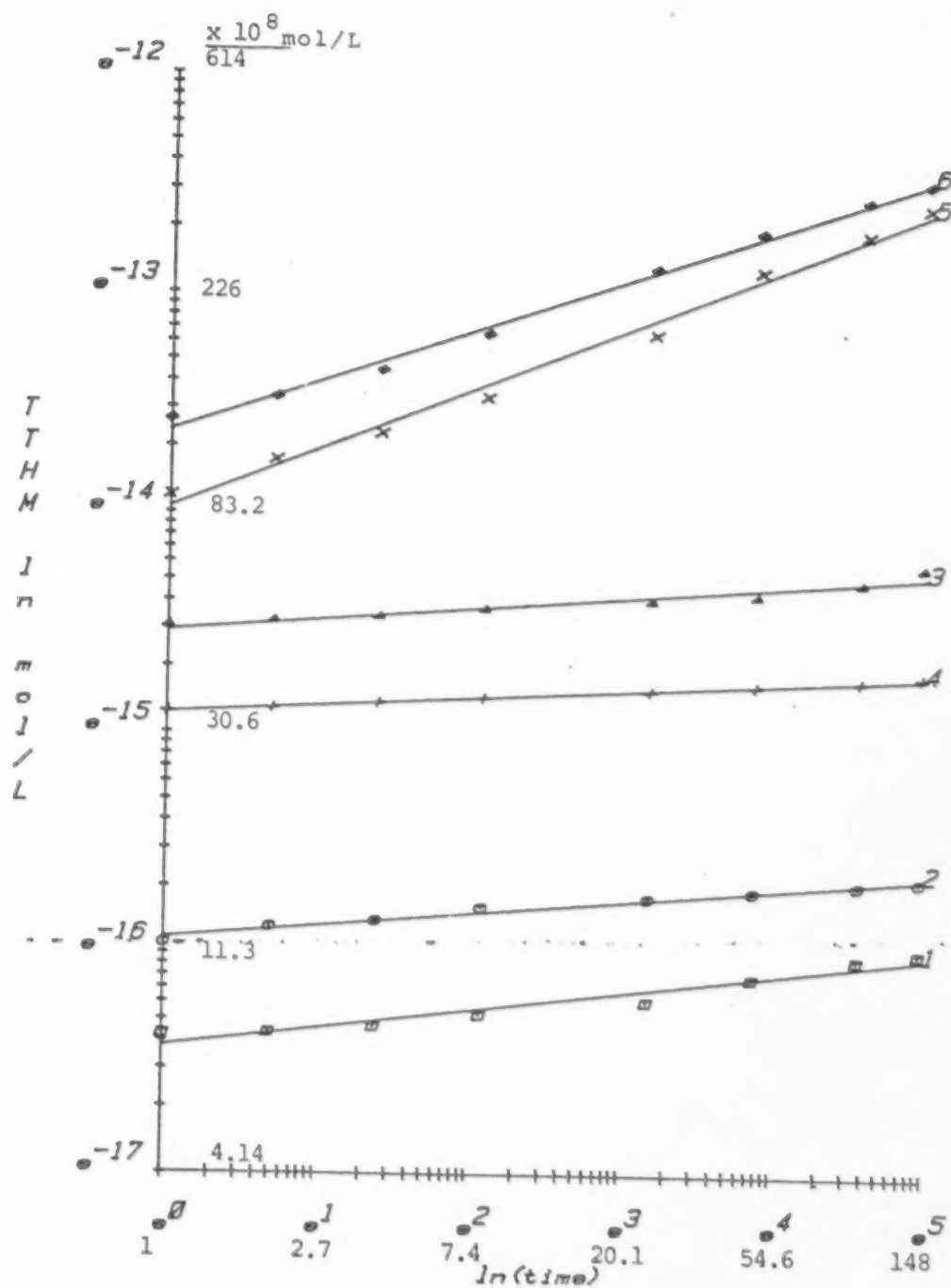


Fig. 4.28. TTHM formation as a function of time at six chlorine concentrations (Phase B, 1×10^{-6} mol/L Bromide, pH 9). (Time in hours.)

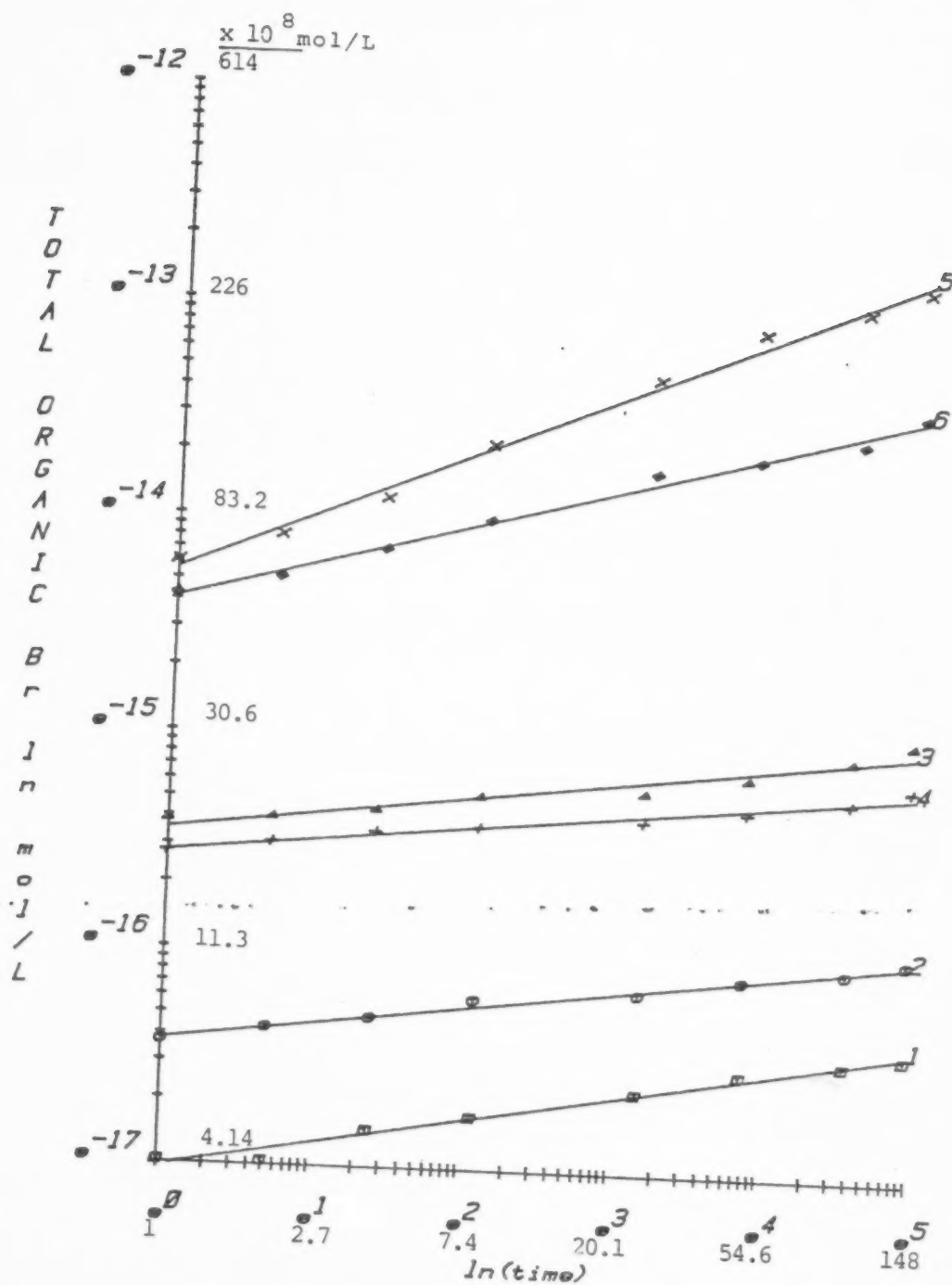


Fig. 4.29. Total organic Br formation as a function of time at six chlorine concentrations (Phase B, $1 \times 10^{-6} \text{ mol/L}$ Bromide, pH 7).

(Time in hours.)

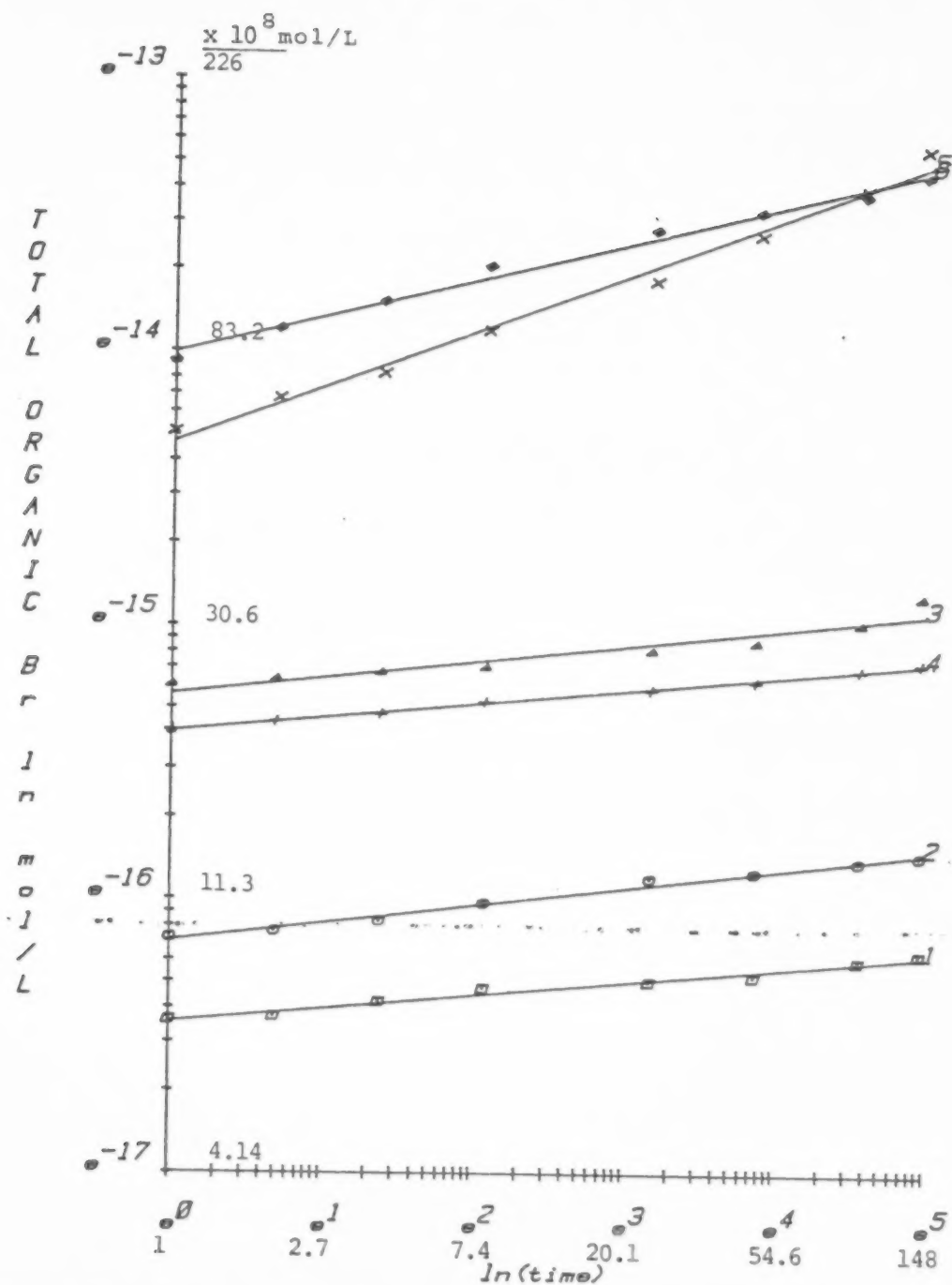


Fig. 4.30. Total organic Br formation as a function of time at six chlorine concentrations (Phase B, 1×10^{-6} mol/L Bromide, pH 9).
(Time in hours.)

concentration 6 total organic Br was 1420×10^{-9} mol/L after 144 hours reaction time at pH 7 and 1590×10^{-9} mol/L at pH 9.

Figures 4.31 and 4.32 show the results of total organic Cl in phase B as a function of time and at six chlorine concentrations, for pH 7 and 9, respectively. The concentration after 144 hours reaction time was below 1640×10^{-9} mol/L for all chlorine concentrations 1, 2, 3 and 4 at both pH 7 and 9. At chlorine concentration 5 the total organic Cl was 6340×10^{-9} mol/L at pH 7 and 8470×10^{-9} mol/L at pH 9 after 144 hours reaction time. At chlorine concentration 6 the concentration was 8360×10^{-9} mol/L at pH 7 and 9690×10^{-9} mol/L at pH 9 after 144 hours reaction time.

The mole ratio of total organic Cl to Br fluctuated at the eight reaction times in experimental phase B. Table 4.15 presents the mole ratio of total organic Cl/Br throughout the eight reaction times in experimental phase B. It appears from the data as though the ratio increases with increasing pH.

The mole percent Br incorporated was calculated based on the addition of 1×10^{-6} mol/L Br^- to groundwater. In general, the mole percent incorporated of Br increased at higher chlorine concentrations and pH, with the exception of chlorine concentration 4 which was at the break point. Table 4.16 presents the mole percent Br incorporated at minimum (1) and maximum (144) hour reaction times in experimental phase B. Incorporation of greater than 100% of the Br^- added indicates a significant contribution of ambient levels of Br^- . Due to the lack of a sensitive method for Br^- determination its concentration was unknown. More recent studies have indicated that the

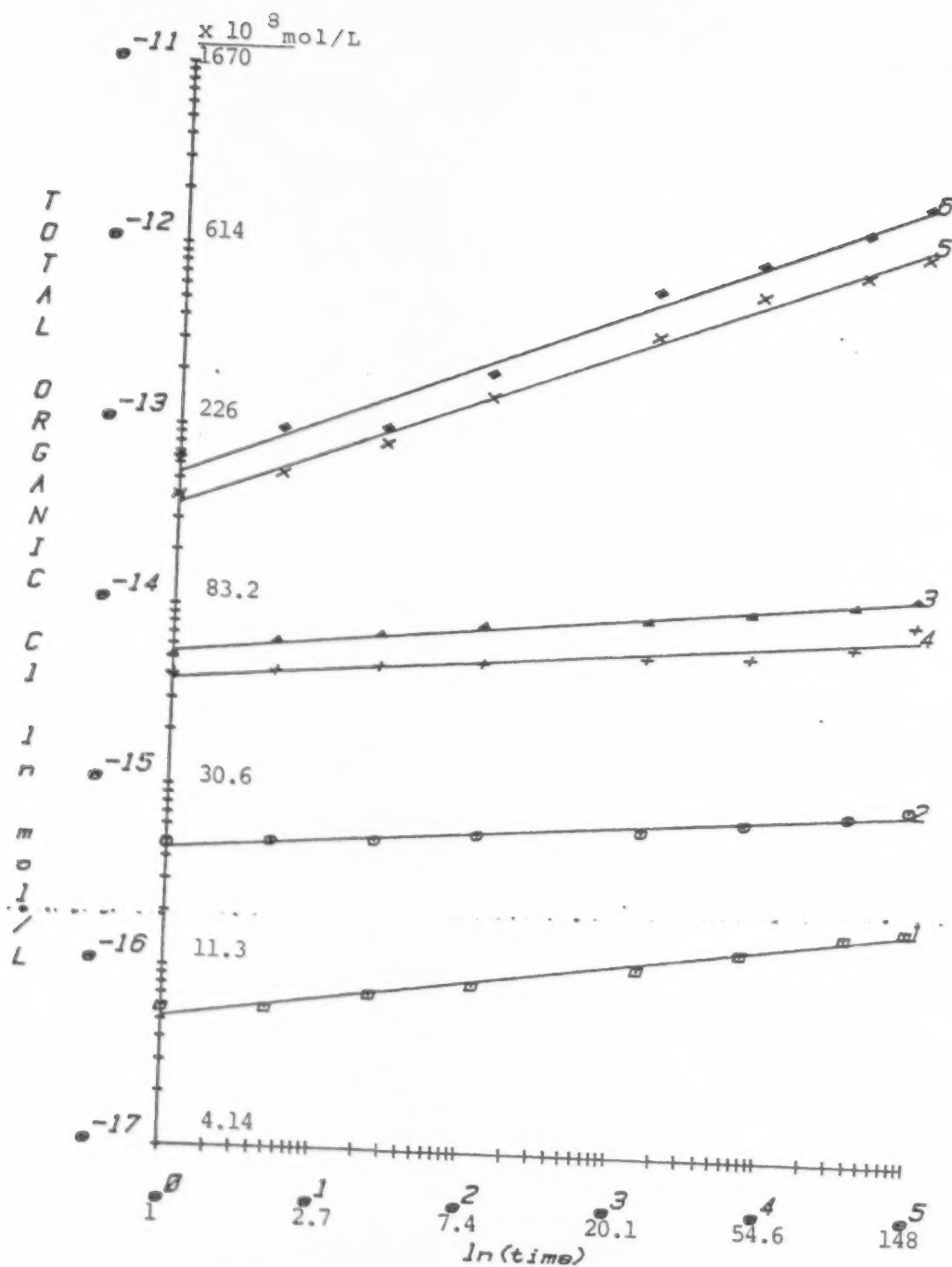


Fig. 4.31. Total organic Cl formation as a function of time at six chlorine concentrations (Phase B, 1×10^{-6} mol/L Bromide, pH 7).

(Time in hours.)

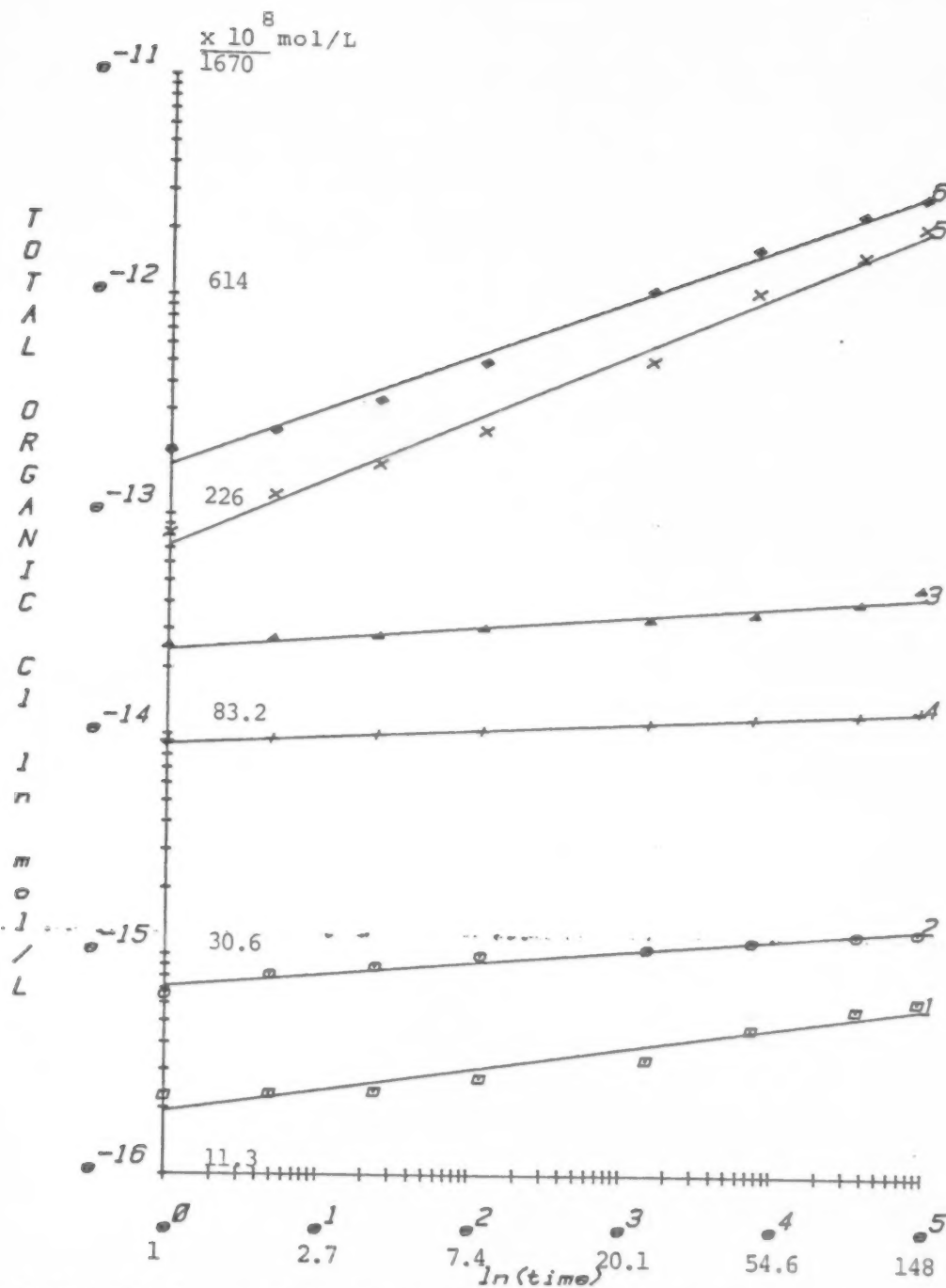


Fig. 4.32. Total organic Cl formation as a function of time at six chlorine concentrations (Phase B, 1×10^{-6} mol/L Bromide, pH 9).

(Time in hours.)

TABLE 4.15

THE MOLE RATIO OF TOTAL ORGANIC Cl/Br THROUGHOUT
EIGHT REACTION TIMES (HOURS) IN EXPERIMENTAL PHASE B.

Chlorine Concentration Number	pH	Range
1	7	1.95 - 2.13
	9	2.13 - 2.70
2	7	2.61 - 3.02
	9	2.30 - 2.80
3	7	3.06 - 3.36
	9	4.80 - 5.13
4	7	3.01 - 3.39
	9	3.49 - 3.87
5	7	3.13 - 4.88
	9	3.36 - 4.93
6	7	3.15 - 5.89
	9	3.68 - 6.09

TABLE 4.16

THE MOLE PERCENT Br INCORPORATED AT MINIMUM (1)
AND MAXIMUM (144) HOURS REACTION TIME IN EXPERIMENTAL
PHASE B.

Chlorine Concentration Number	pH	Reaction Time (hours)	
		1	144
1	7	4.20	7.36
	9	7.23	9.29
2	7	9.79	13.7
	9	9.77	13.3
3	7	20.2	31.3
	9	24.5	34.2
4	7	17.5	24.5
	9	20.8	26.9
5	7	48.6	130
	9	61.9	175
6	7	57.4	142
	9	80.2	159

Br^- concentration may be as high as 4×10^{-6} mol/L (Amy, 1983).

In general, the mole percent Cl incorporated increased at higher chlorine concentrations and pH. Table 4.17 presents the mole percent Cl incorporated of Cl at minimum (1) and maximum (144) hours reaction time in experimental phase B. The highest percentage incorporated was 2.54.

Experimental Phase C: The condition designated for this phase was the addition of 1×10^{-5} mol/L Br^- to the sample of groundwater prior to chlorination. The formation and distribution of THM's was investigated as a function of time, pH and chlorine concentration. The chlorine concentrations used in phase C were given in Table 4.6 and shown in Figure 4.3.

The concentration of CHCl_3 as a function of time and chlorine concentration is shown in Figure 4.33 and 4.34, for pH 7 and 9, respectively. In the presence of 1×10^{-5} mol/L Br^- , chloroform is the predominant trihalomethane formed at chlorine concentrations 1, 2, 3 and 4, but, at chlorine concentrations 5 and 6 after the breakpoint, the relative concentration decreases.

The concentration of chloroform increased from chlorine concentrations 1 to 3, decreased at chlorine concentration 4 and increased again at 5 and 6. At pH 9 the concentration CHCl_3 , was higher than the corresponding pH 7 value.

The slope of the curves (rate of formation) in Figure 4.33 and 4.34, were similar at both pH levels. At chlorine concentrations 1 through 6 CHCl_3 increased in concentration with time at both pH levels, the slope (rate) was greater at pH 9 than at pH 7.

TABLE 4.17

THE MOLE PERCENT Cl INCORPORATED AT MINIMUM (1)
AND MAXIMUM (144) HOURS REACTION TIME IN EXPERIMENTAL
PHASE B.

Chlorine Concentration Number	pH	Reaction Time (hours)	
		1	144
1	7	0.316	0.539
	9	0.571	0.890
2	7	0.261	0.353
	9	0.301	0.405
3	7	0.370	0.567
	9	0.734	0.970
4	7	0.250	0.368
	9	0.356	0.416
5	7	0.456	1.90
	9	0.625	2.54
6	7	0.377	1.68
	9	0.605	1.94

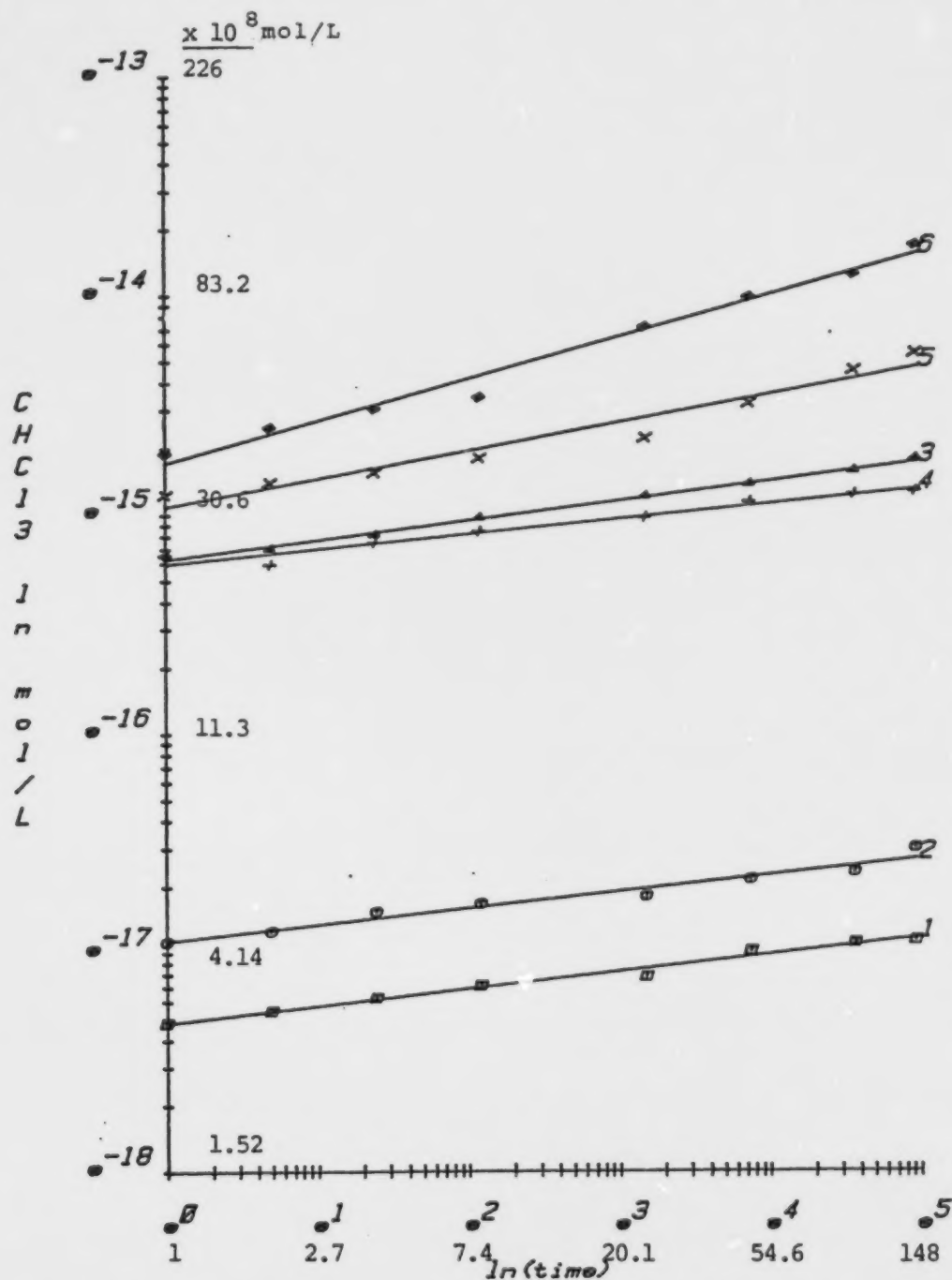


Fig. 4.33. CHCl_3 formation as a function of time at six chlorine concentrations (Phase C, 1×10^{-5} mol/L Bromide pH 7). (Time in hours.)

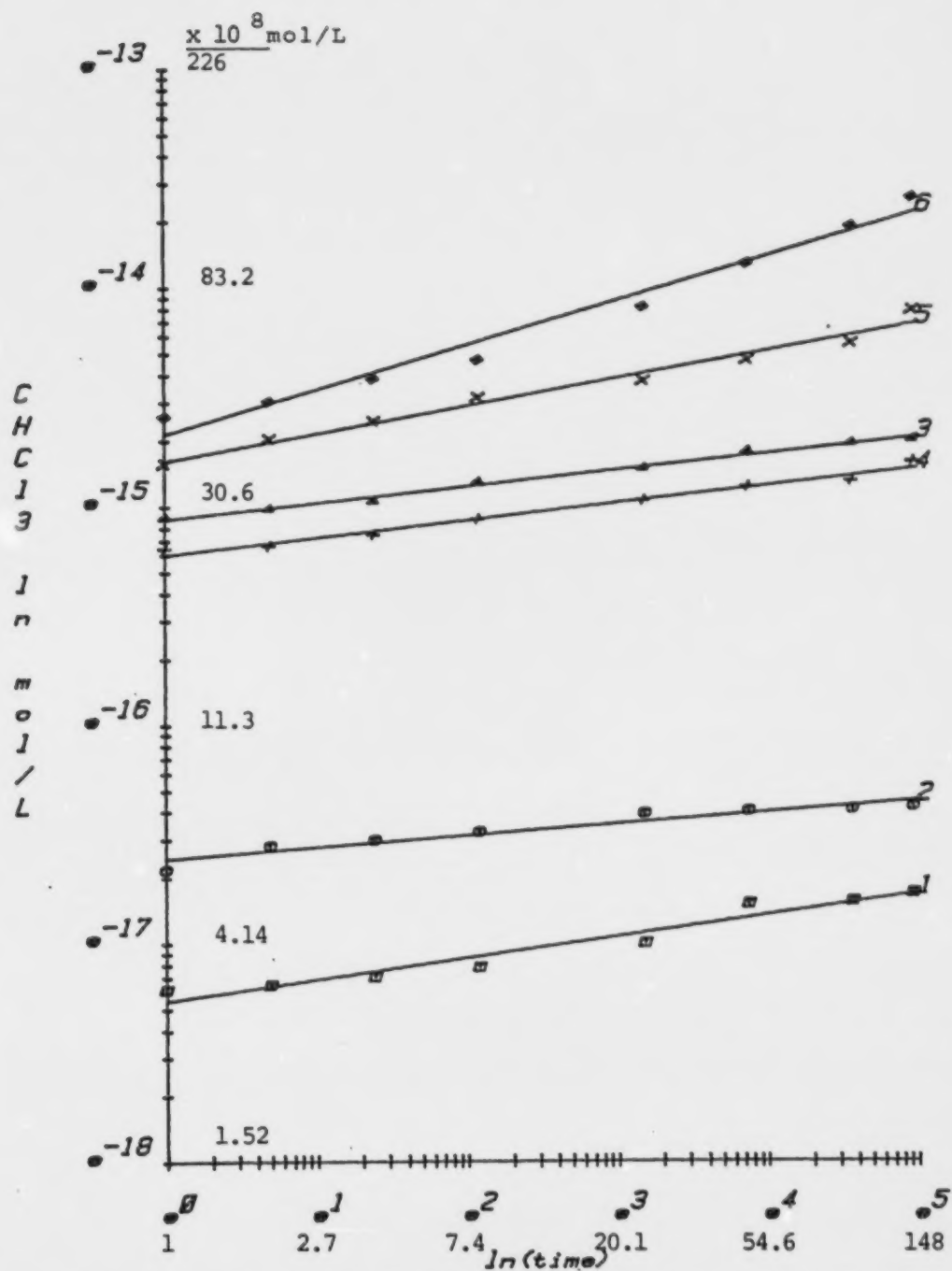


Fig. 4.34. CHCl_3 formation as a function of time at six chlorine concentrations (Phase C, 1×10^{-5} mol/L Bromide pH 9). (Time in hours.)

Figures 4.35 and 4.36 show the results of CHCl_2Br formation in phase C as a function of time, and at six chlorine concentrations, for pH 7 and 9, respectively.

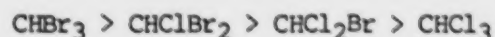
Figures 4.37 and 4.38 show the result of CHClBr_2 formation in phase C as a function of time, and at six chlorine concentrations, for pH 7 and 9, respectively.

Figures 4.39 and 4.40 show the results of CHBr_3 formation in phase C as a function of time, and at six chlorine concentrations, for pH 7 and 9, respectively.

It should be noted that the yield of CHBr_3 was much higher in experimental phase C relative to experimental phase A and B.

Longer reaction times, higher chlorine concentration and higher pH led to an increased concentration of THM's. The exception as above was chlorine concentration 4, which was the break point where a minimum free residual of chlorine exists.

Examination of data reveals that the addition of 1×10^{-5} mol/L Br^- to groundwater caused a significant increase in the yield of brominated THM's at chlorine concentrations 5 and 6, the relative THM concentration at chlorine concentrations 5 and 6 were:



Figures 4.41 and 4.42 show the results of TTHM formation in phase C as a function of time and chlorine concentration, at pH 7 and 9, respectively. TTHM concentration increased with time, chlorine concentration and pH with the exception of chlorine concentration 4, which was the break point.

Figures 4.43 and 4.44 show the results of total organic Br in phase

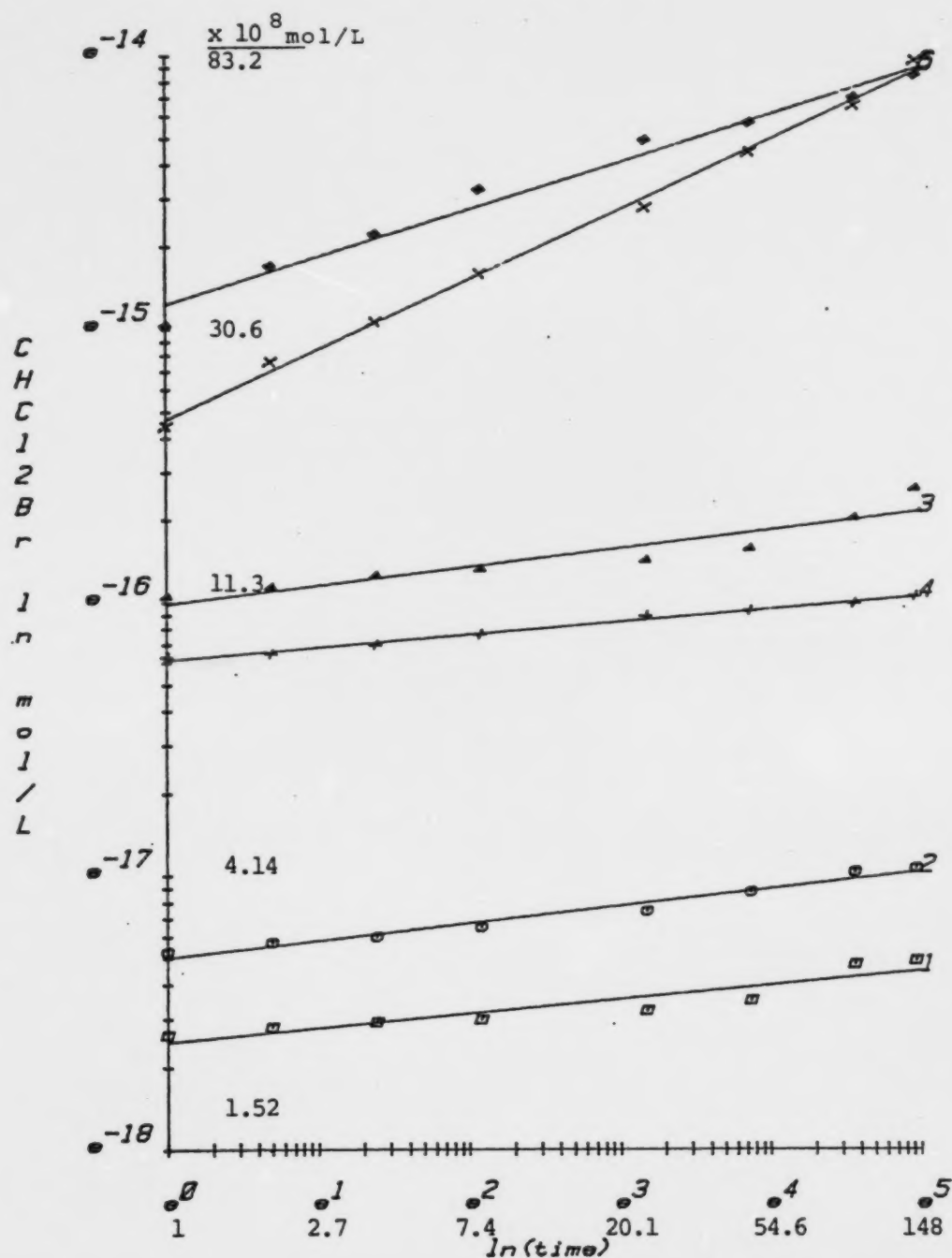


Fig. 4.35. CHCl_2Br formation as a function of time at six chlorine concentrations (Phase C, $1 \times 10^{-5} \text{ mol/L}$ Bromide, pH 7). (Time in hours.)

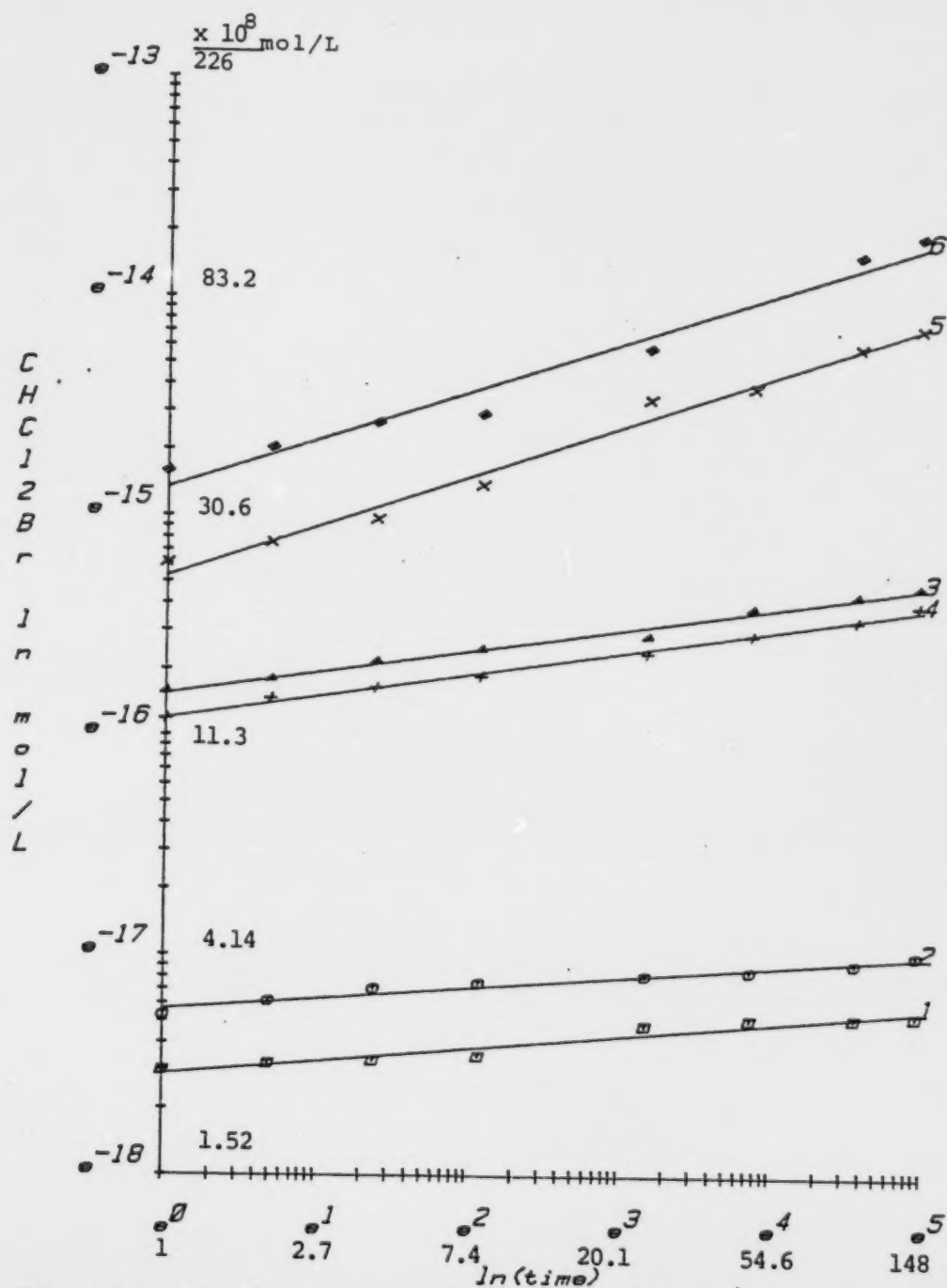


Fig. 4.36. CHCl_2Br formation as a function of time at six chlorine concentrations (Phase C, $1 \times 10^{-5} \text{ mol/L}$ Bromide, pH 9). (Time in hours.)

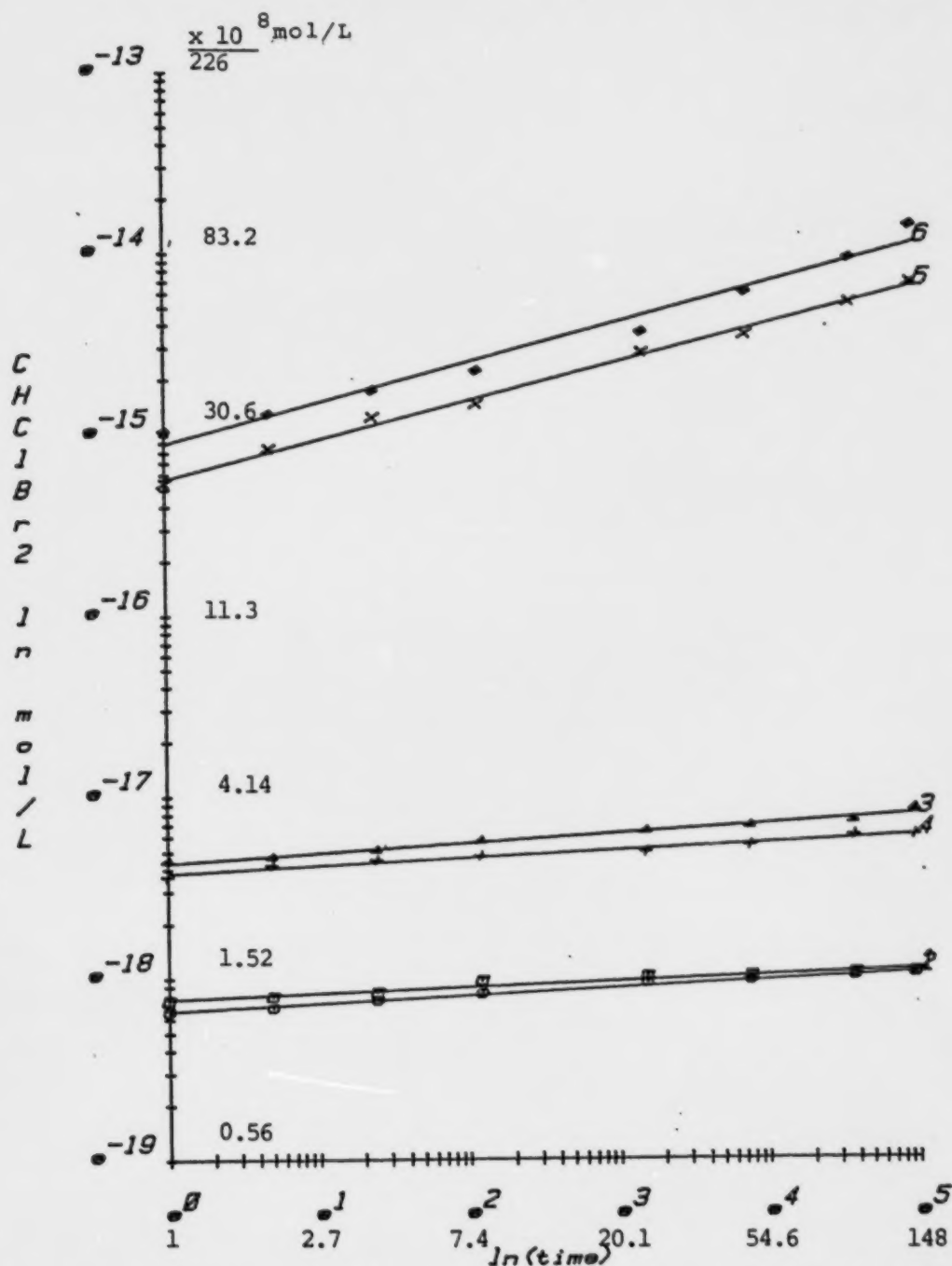


Fig. 4.37. CHClBr_2 formation as a function of time at six chlorine concentrations (Phase C, $1 \times 10^{-5} \text{ mol/L}$ Bromide, pH 7).

(Time in hours.)

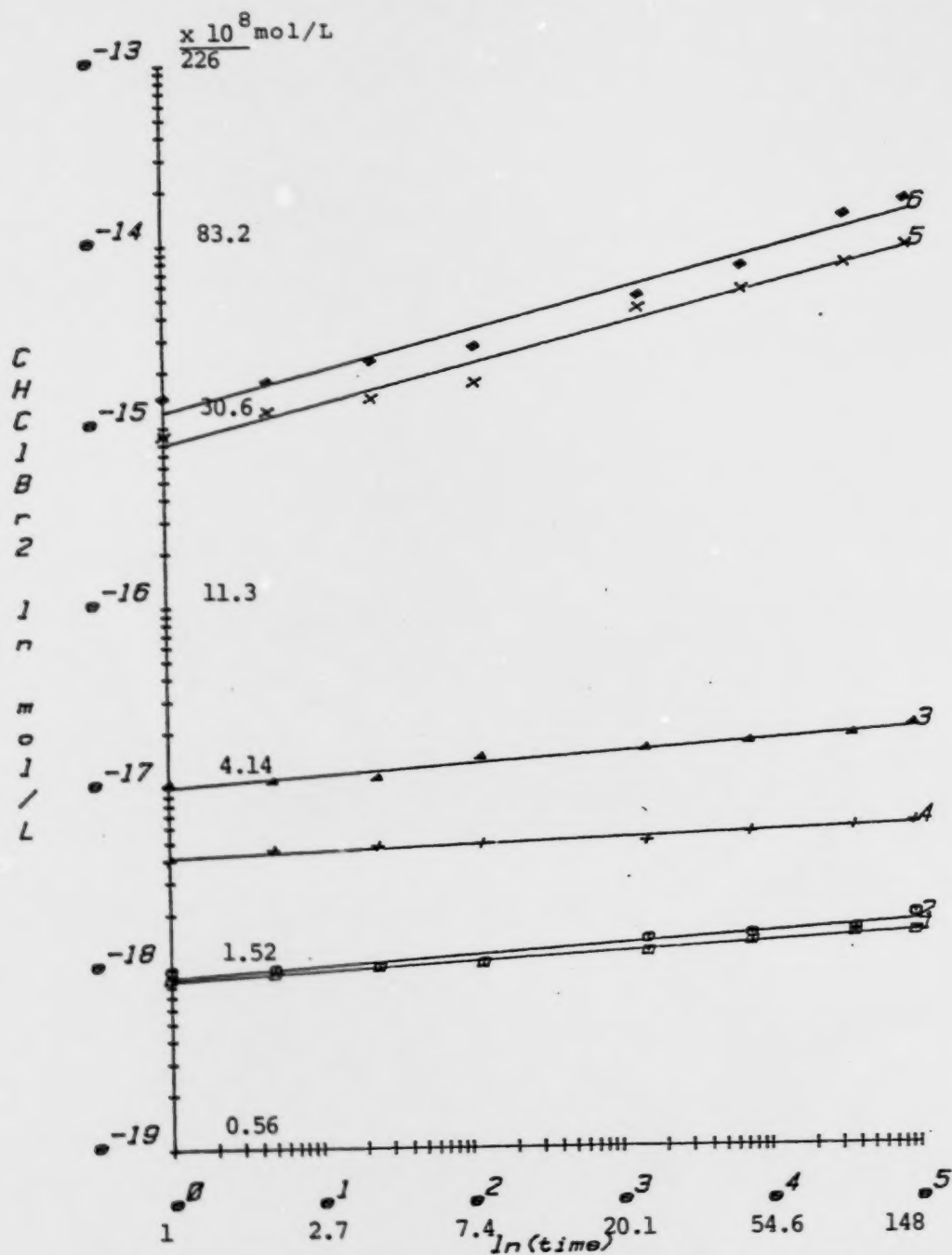


Fig. 4.38. CHClBr_2 formation as a function of time at six chlorine concentrations (Phase C, 1×10^{-5} mol/L Bromide, pH 9). (Time in hours.)

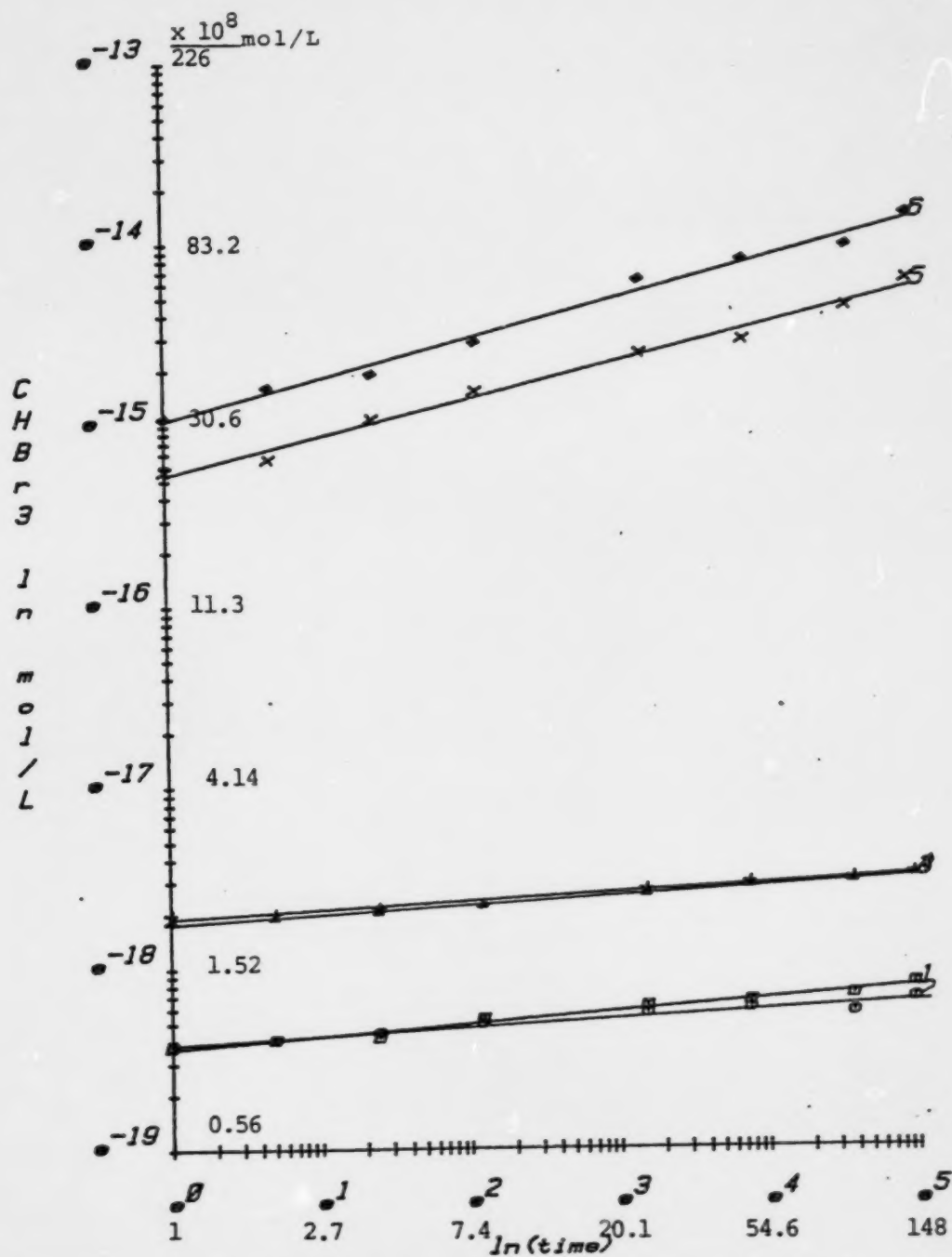


Fig. 4.39. CHBr_3 formation as a function of time at six chlorine concentrations (Phase C, 1×10^{-5} mol/L Bromide, pH 7).
(Time in hours.)

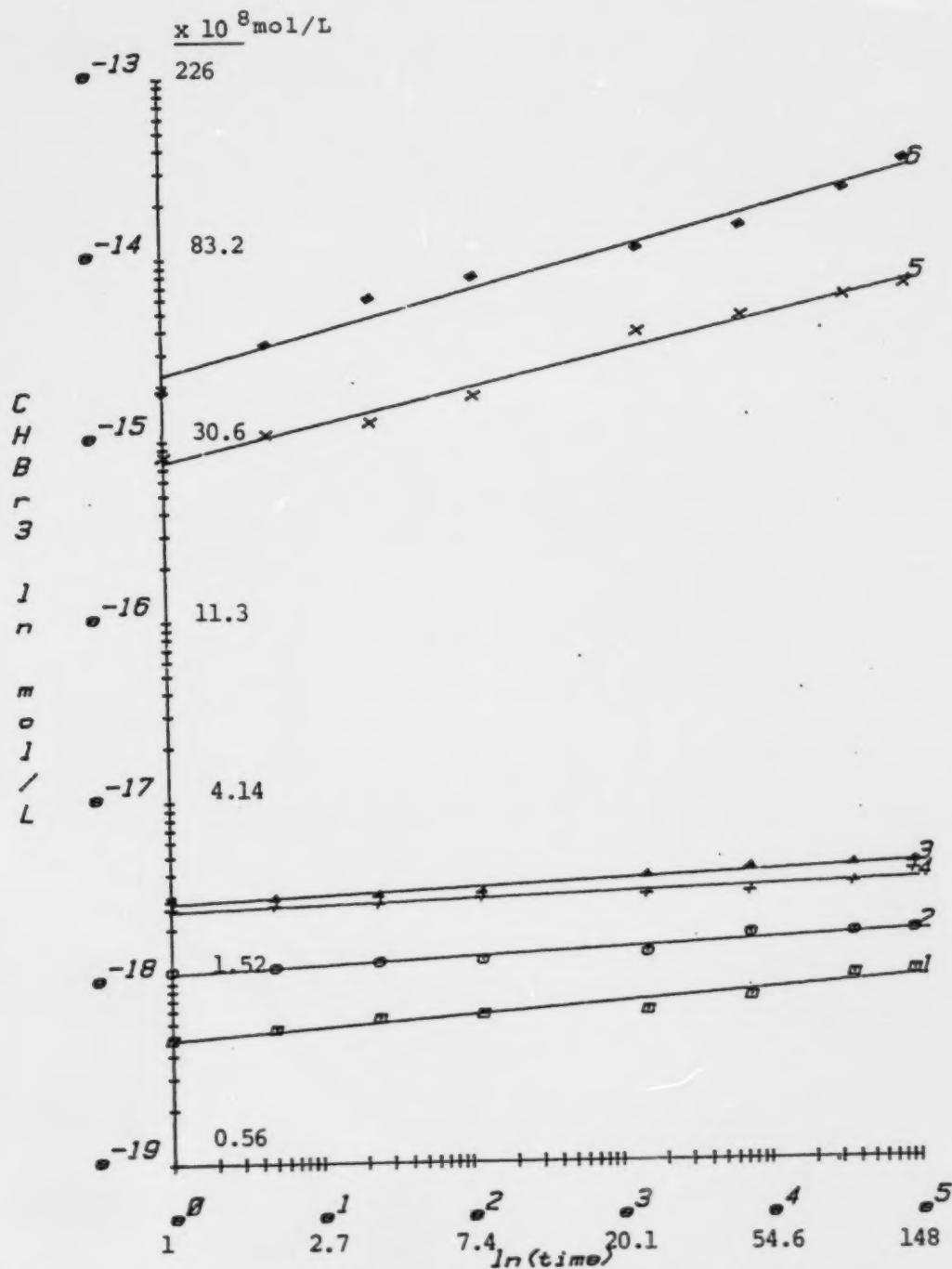


Fig. 4.40. CHBr_3 formation as a function of time at six chlorine concentrations (Phase C, 1×10^{-5} mol/L Bromide, pH 9).
(Time in hours.)

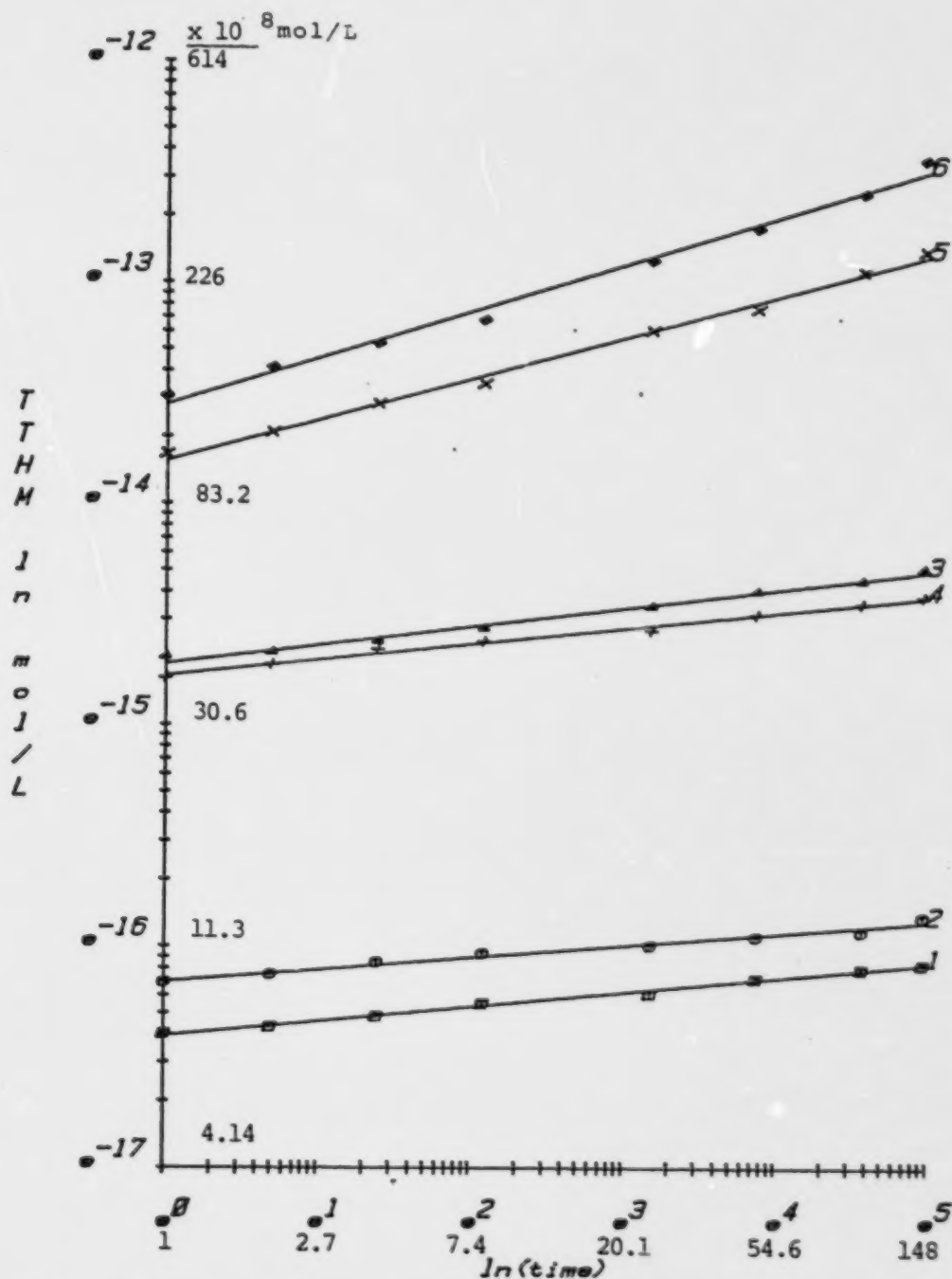


Fig. 4.41. THM formation as a function of time at six chlorine concentrations (Phase C, 1×10^{-5} mol/L Bromide, pH 7). (Time in hours.)

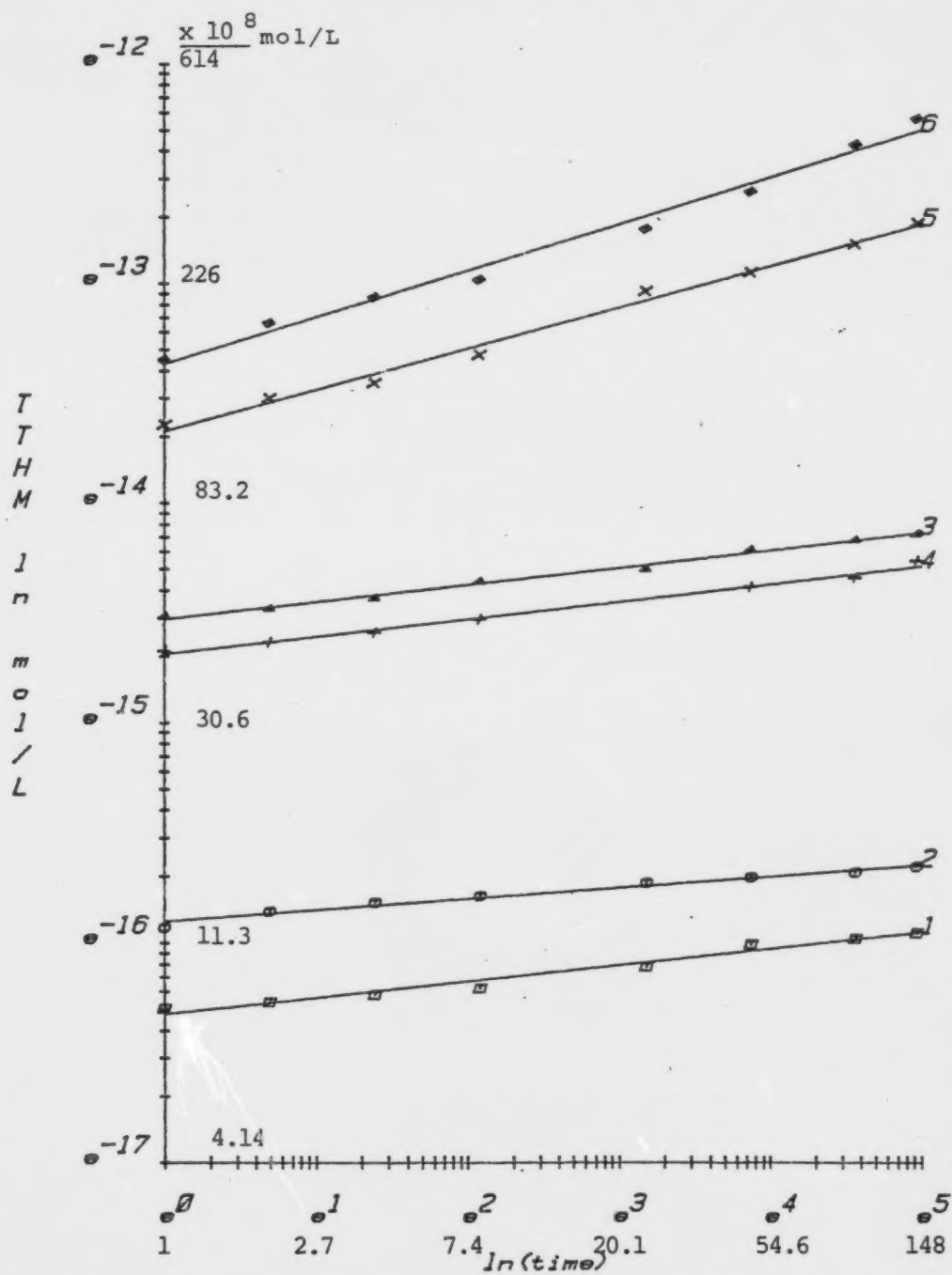


Fig. 4.42. THM formation as a function of time at six chlorine concentrations (Phase C, 1×10^{-5} mol/L Bromide, pH 9). (Time in hours.)

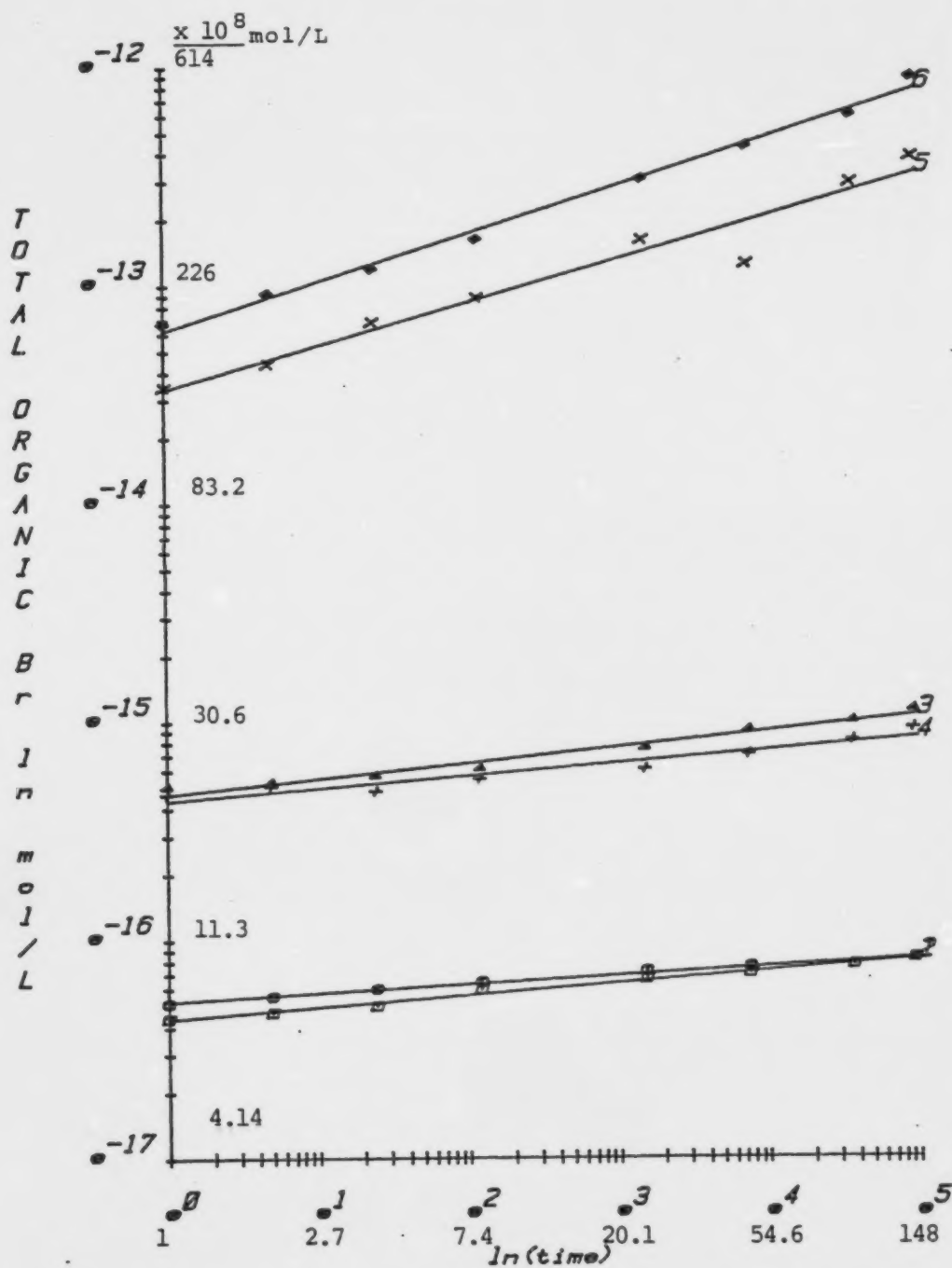


Fig. 4.43 Total organic Br formation as a function of time at six chlorine concentrations (Phase C, 1×10^{-5} mol/L Bromide, pH 7).

(Time in hours.)

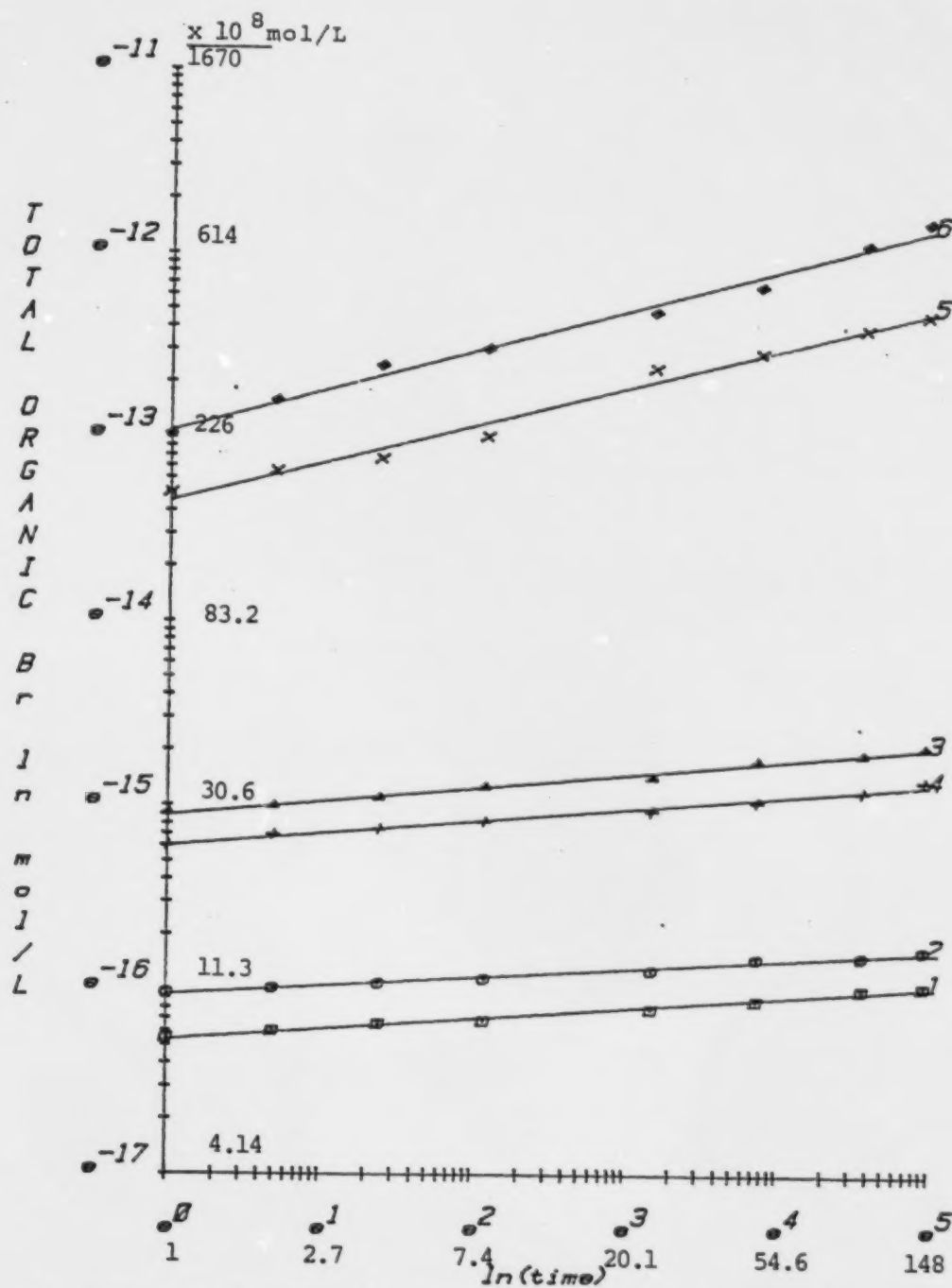


Fig. 4.44. Total organic Br formation as a function of time at six chlorine concentrations (Phase C, 1×10^{-5} mol/L Bromide, pH 9).

(Time in hours.)

C as a function of time, and at six chlorine concentrations, for pH 7 and 9, respectively. The concentration of total organic Br was significantly higher relative to phase A and B due to the addition of 1×10^{-5} mol/L Br^- to the groundwater sample. The concentration of total organic Br at 144 hours reaction time was below 424×10^{-9} mol/L at chlorine concentrations 1, 2, 3 and 4 at both pH 7 and 9. At chlorine concentration 5 after 144 hours reaction time it was 4000×10^{-9} mol/L at pH 7 and 4410×10^{-9} mol/L at pH 9. At chlorine concentration 6 total organic Br was 5750×10^{-9} mol/L at 144 hours reaction time at pH 7 and 7300×10^{-9} mol/L at pH 9.

Figures 4.45 and 4.46 show the results of total Cl in phase C as a function of time, and at six chlorine concentrations, for pH 7 and 9, respectively. The total organic Cl concentration at 144 hours reaction time was below 1740×10^{-9} mol/L at chlorine concentrations 1, 2, 3 and 4 at both pH 7 and 9. At chlorine concentration 5 the total organic Cl was 3820×10^{-9} mol/L at pH 7 and 4480×10^{-9} mol/L at pH 9 after 144 hours reaction time. At chlorine concentration 6 the concentration was $6030 \text{ mol/L} \times 10^{-9}$ at pH 7 and $6950 \text{ mol/L} \times 10^{-9}$ at pH 9 after 144 hours reaction time.

The mole ratio of total organic Cl to Br fluctuated differently throughout the eight reaction times in experimental phase C. Table 4.18 presents the mole ratio of total organic Cl/Br throughout the eight reaction times in experimental phase C. At this concentration of Br^- the effect of an increased incorporation of Br into the organic function is reflected in a decrease of the mole ratio Cl/Br at chlorine concentrations 5 and 6.

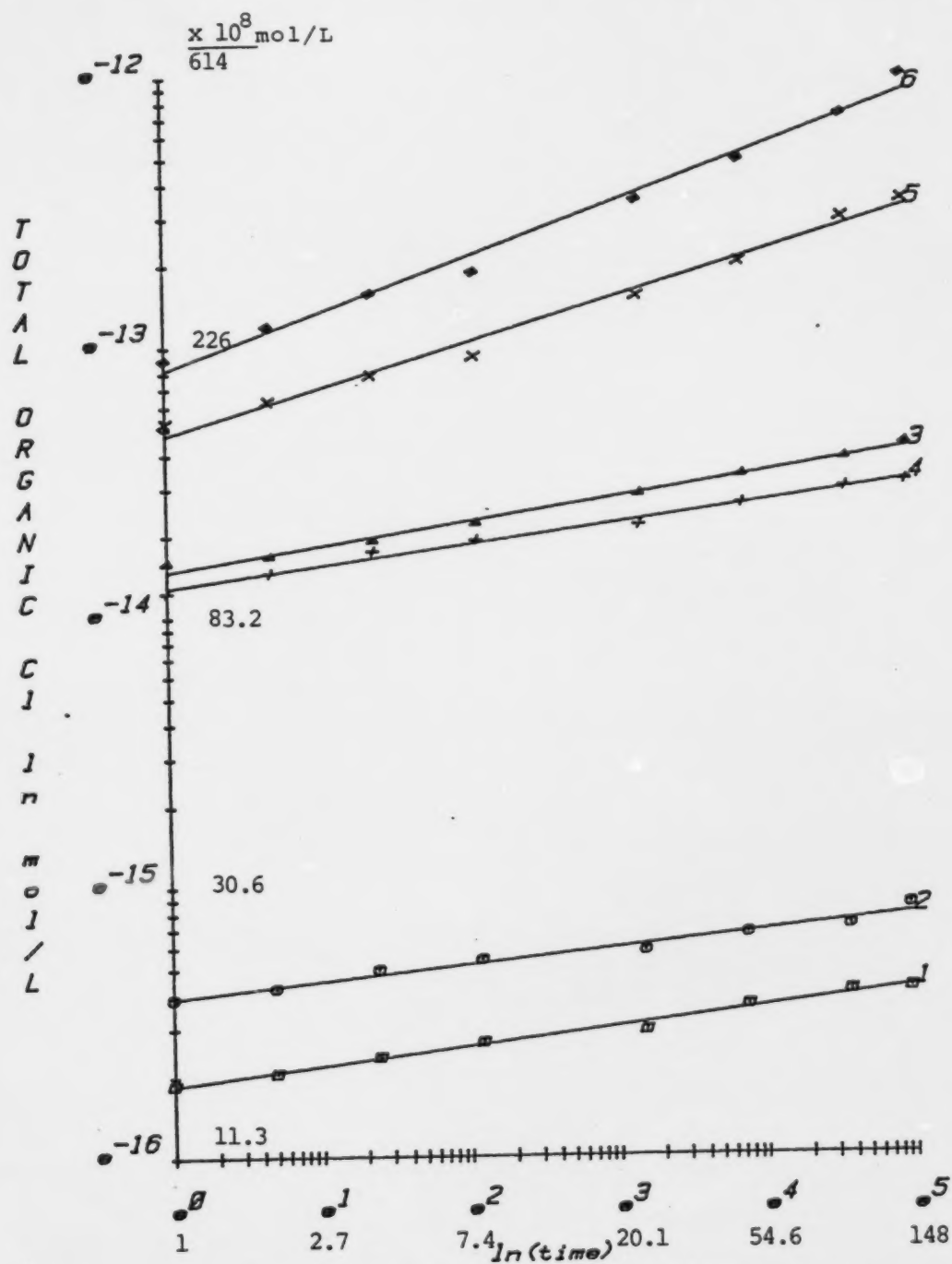


Fig. 4.45. Total organic Cl formation as a function of time at six chlorine concentrations (Phase C, 1×10^{-5} mol/L Bromide, pH 7).

(Time in hours.)

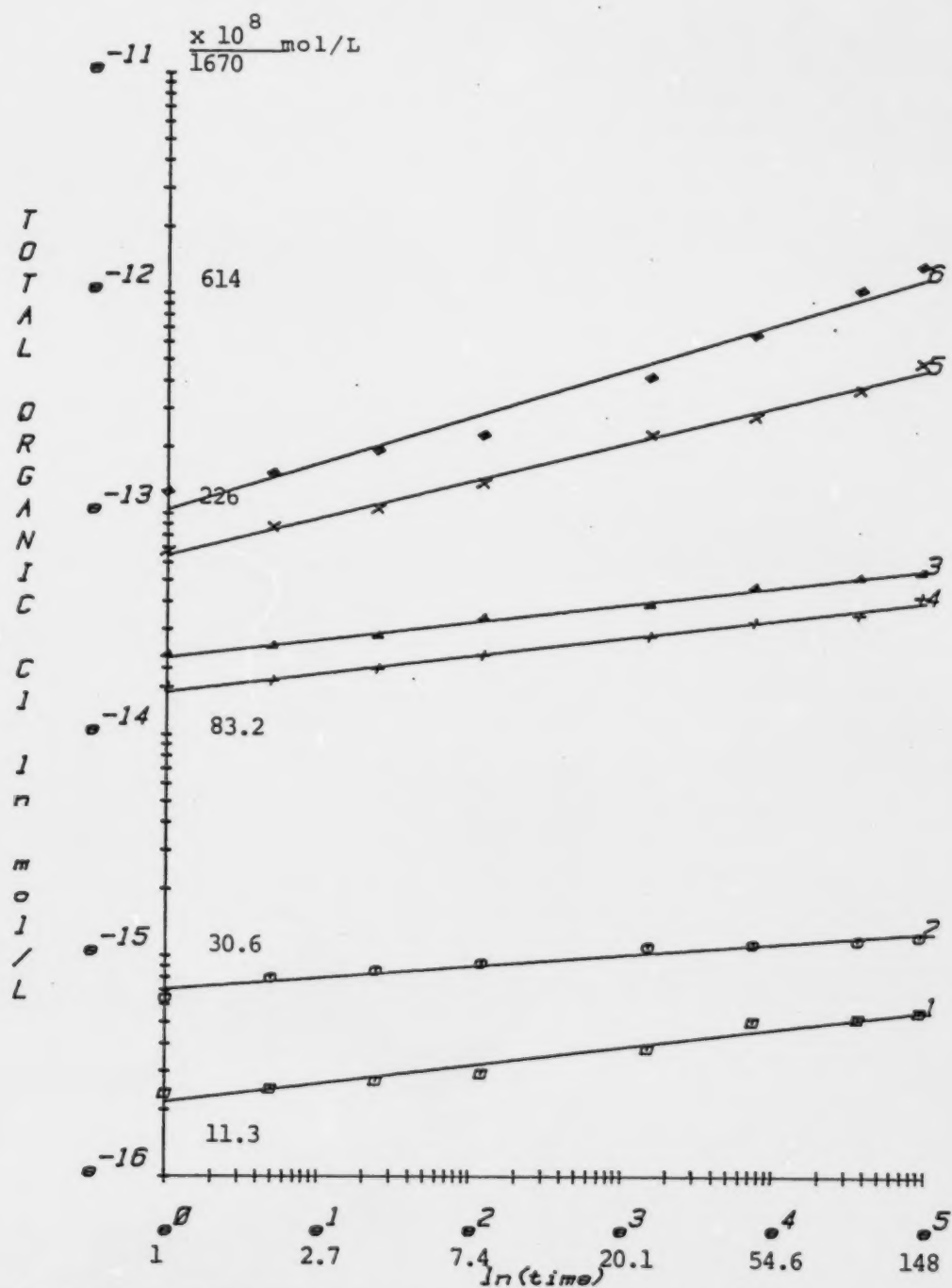


Fig. 4.46. Total organic Cl formation as a function of time at six chlorine concentrations (Phase C, 1×10^{-5} mol/L Bromide, pH 9).
(Time in hours.)

TABLE 4.18

THE MOLE RATIO OF TOTAL ORGANIC Cl/Br THROUGHOUT
EIGHT REACTION TIMES (HOURS) IN EXPERIMENTAL PHASE C.

Chlorine Concentration Number	pH	Range
1	7	1.87 - 2.06
	9	1.86 - 2.13
2	7	2.39 - 2.75
	9	2.28 - 2.53
3	7	4.47 - 4.83
	9	4.05 - 4.17
4	7	4.15 - 4.75
	9	4.05 - 4.40
5	7	0.955 - 1.23
	9	0.973 - 1.15
6	7	1.05 - 1.14
	9	0.904 - 1.09

The mole percent Br incorporated was calculated based on the addition of 1×10^{-5} mol/L Br^- to ground water. In general, the percent of Br incorporated increased due to higher chlorine concentration, the addition of 1×10^{-5} mol/L Br^- to groundwater and higher pH. Table 4.19 presents the mole percent Br incorporated at minimum (1) and maximum (144) hour reaction times in experimental phase C. The ambient level of Br^- may cause a higher percent incorporation than would be expected. Again, because the concentration is unknown it is impossible to correct for it in the calculations.

In general the mole percent Cl incorporated increased due to higher chlorine concentrations and pH with the exception of chlorine concentration 4 which was at the break point. Table 4.20 presents the mole percent Cl incorporated at minimum (1) and maximum (144) hours reaction times in experimental phase C.

Experimental Phase D: The condition designated for this phase was the addition of 1×10^{-4} mol/L Br^- to the sample of groundwater prior to chlorination. The formation and distribution of THM's was investigated as a function of time, pH and chlorine concentration. The chlorine concentration used in phase D are given in Table 4.7 and shown in Figure 4.4.

The concentration of CHCl_3 as a function of time and at six chlorine concentrations is shown in Figure 4.47 and 4.48 for pH 7 and 9, respectively. In the presence of 1×10^{-4} mol/L Br^- a substantial reduction in chloroform concentration was observed.

Figures 4.49 and 4.50 show the results of CHCl_2Br formation in

TABLE 4.19

THE MOLE PERCENT Br INCORPORATED AT MINIMUM (1)
AND MAXIMUM (144) HOURS REACTION TIME IN EXPERIMENTAL
PHASE C.

Chlorine Concentration Number	pH	Reaction Time (hours)	
		1	144
1	7	0.790	1.03
	9	0.869	1.16
2	7	0.848	1.03
	9	1.11	1.41
3	7	2.28	3.21
	9	2.94	4.24
4	7	2.20	2.95
	9	2.46	3.55
5	7	14.2	40.0
	9	16.7	44.1
6	7	19.0	57.5
	9	23.0	73.0

TABLE 4.20

THE MOLE PERCENT Cl INCORPORATED AT MINIMUM (1)
AND MAXIMUM (144) HOURS REACTION TIME IN EXPERIMENTAL
PHASE C.

Chlorine Concentration Number	pH	Reaction Time (hours)	
		1	144
1	7	0.525	0.738
	9	0.582	0.844
2	7	0.192	0.267
	9	0.239	0.316
3	7	0.557	0.847
	9	0.650	0.951
4	7	0.404	0.597
	9	0.456	0.690
5	7	0.506	1.13
	9	0.565	1.33
6	7	0.425	1.19
	9	0.492	1.37

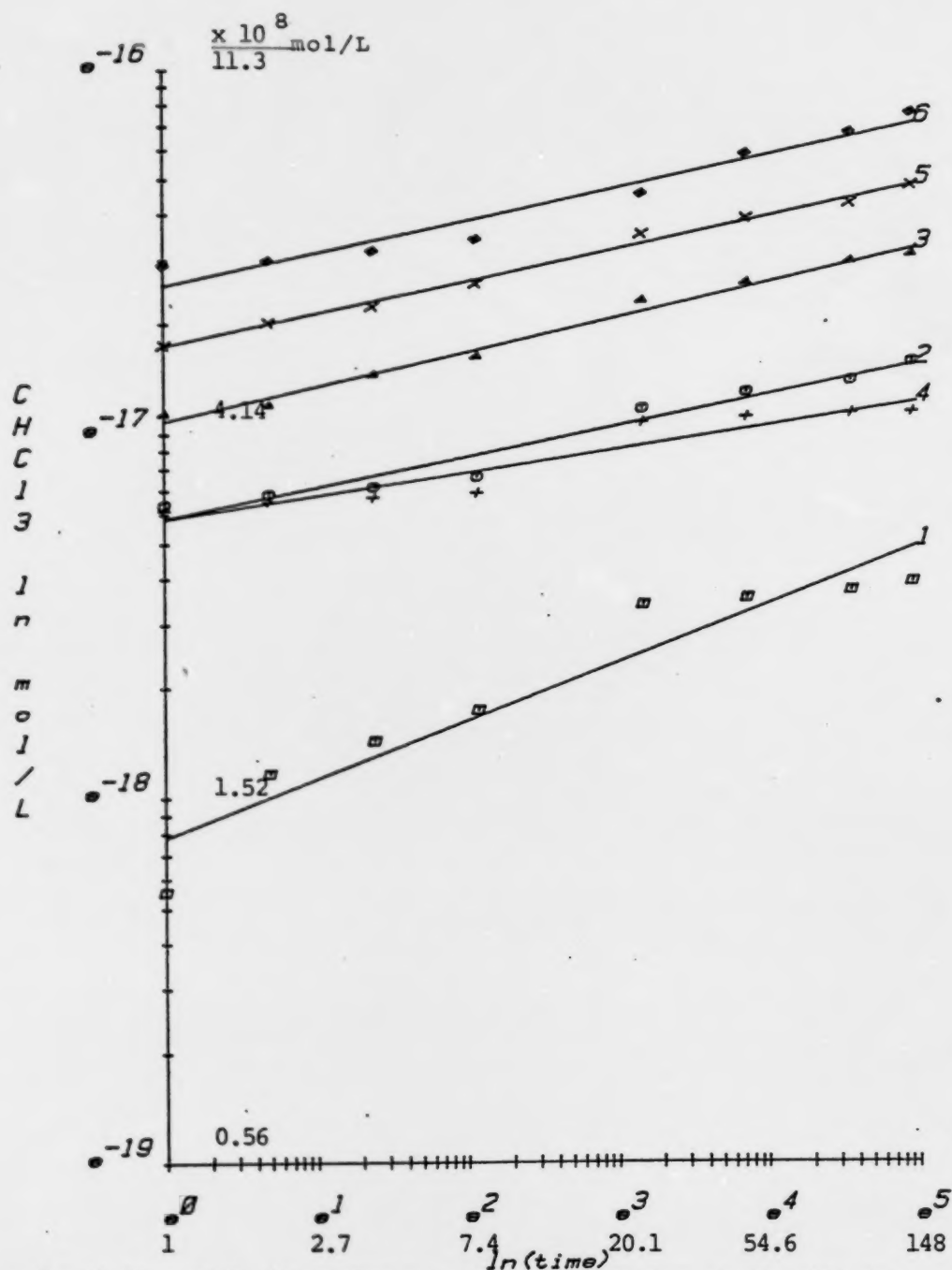


Fig. 4.47. CHCl_3 formation as a function of time at six chlorine concentrations (Phase D, 1×10^{-4} mol/L Bromide, pH 7).

(Time in hours.)

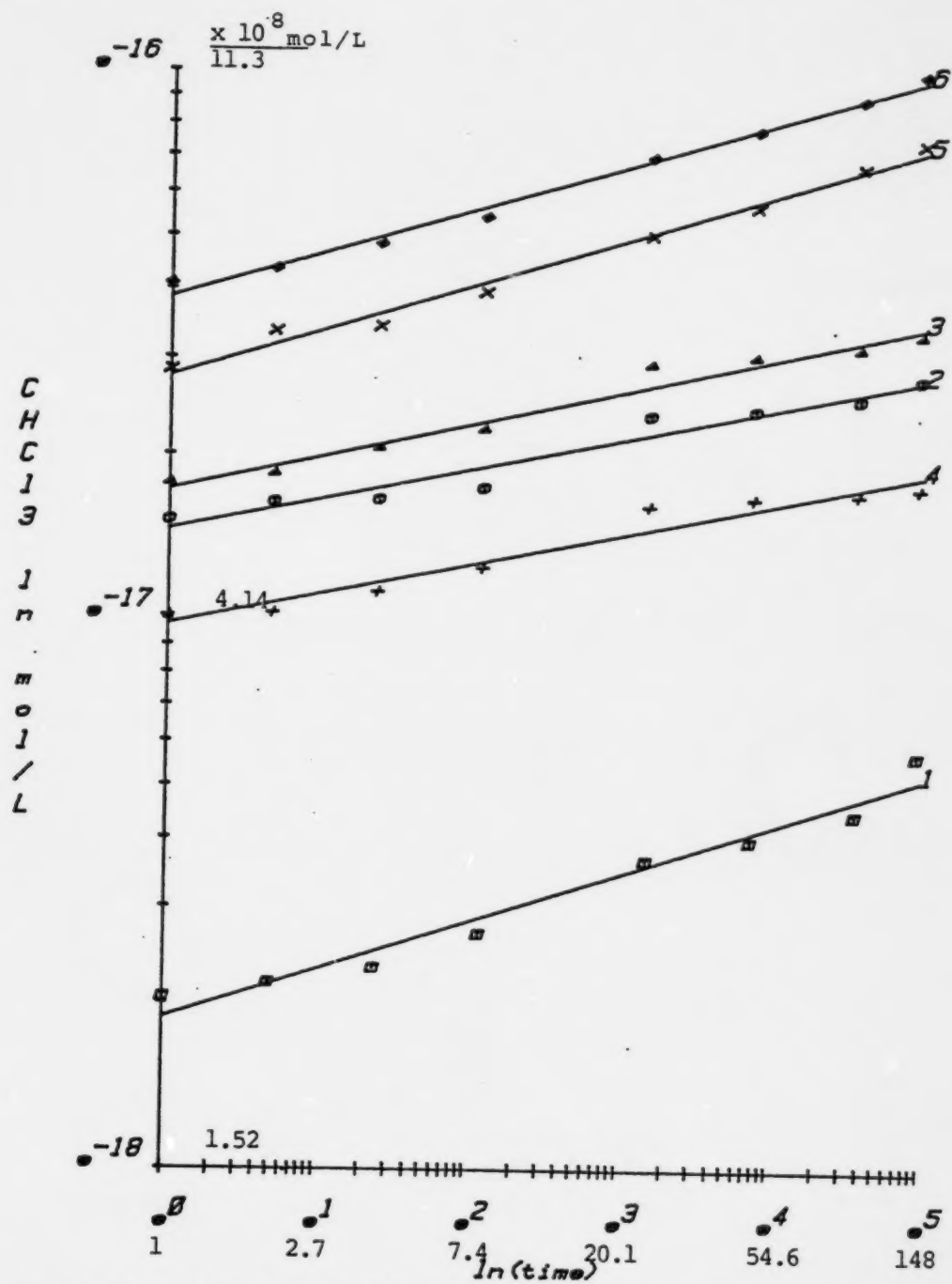


Fig. 4.48. CHCl_3 formation as a function of time at six chlorine concentrations (Phase D, 1×10^{-4} mol/L Bromide, pH 9). (Time in hours.)

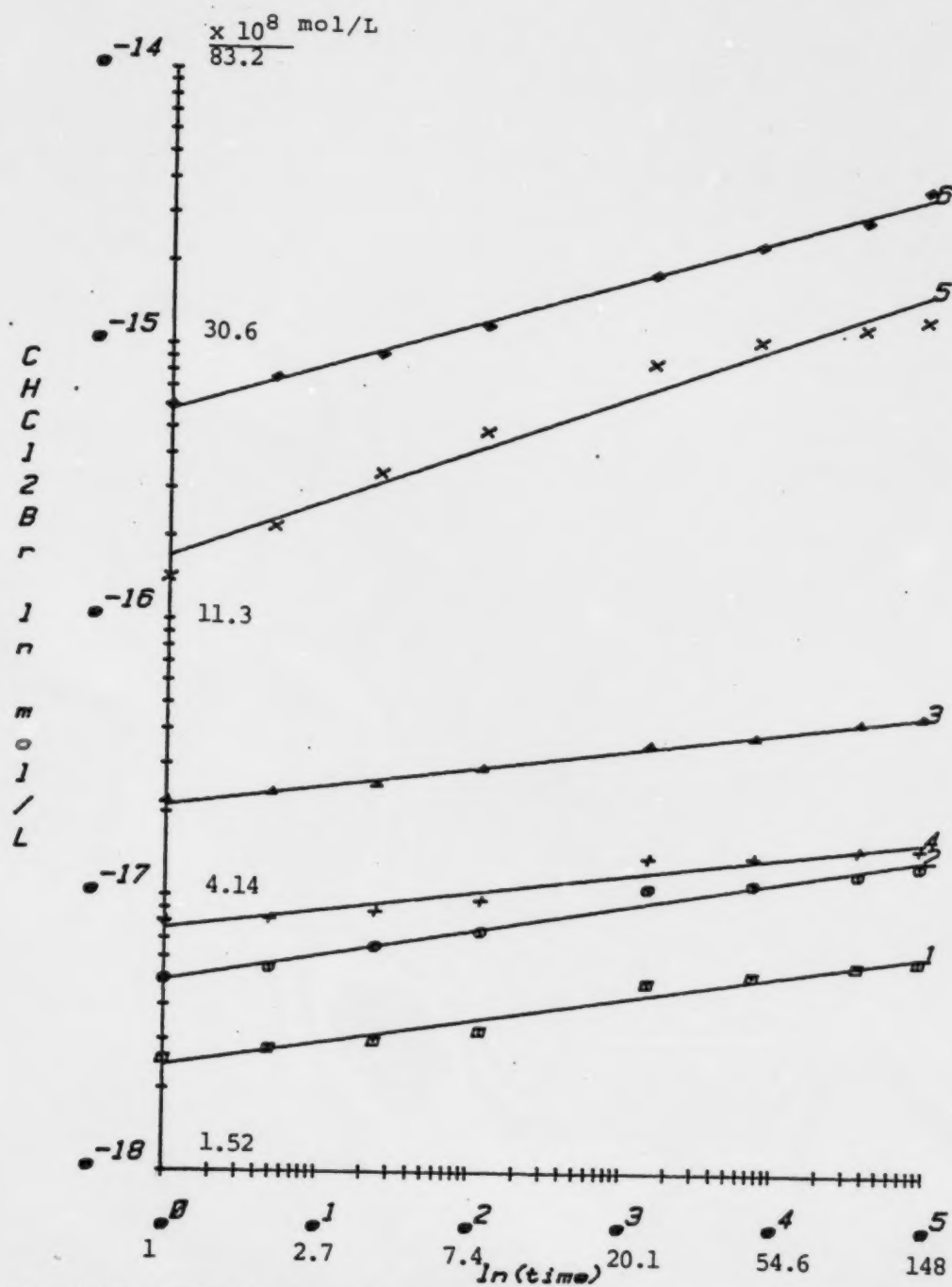


Fig. 4.49. CHCl_2Br formation as a function of time at six chlorine concentrations (Phase D, $1 \times 10^{-4} \text{ mol/L}$ Bromide, pH 7). (Time in hours.)

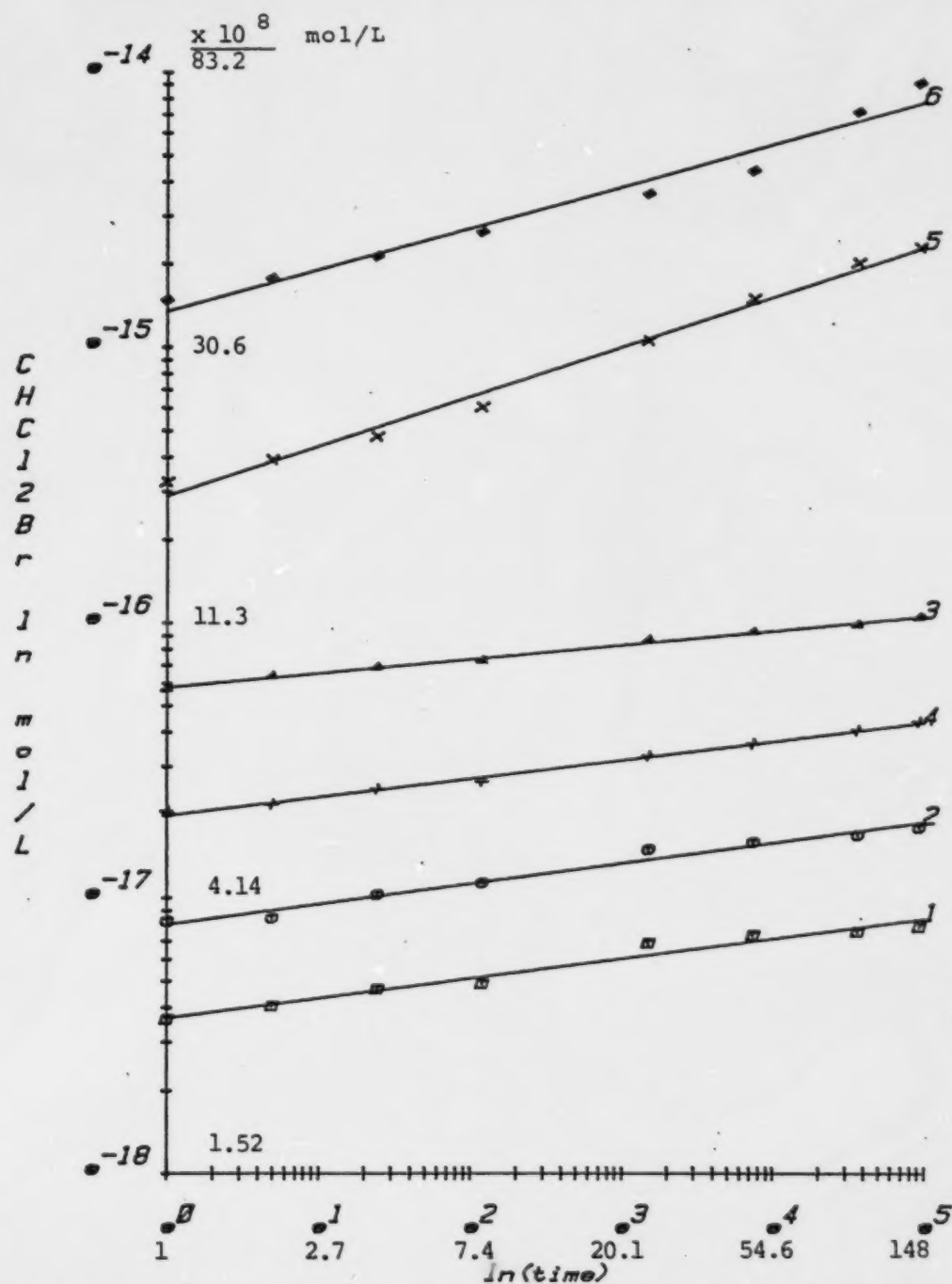


Fig. 4.50. CHCl_2Br formation as a function of time at six chlorine concentrations (Phase D, 1×10^{-4} mol/L Bromide, pH 9).

(Time in hours.)

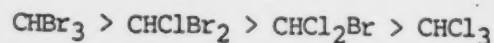
phase D as a function of time, at six chlorine concentrations, for pH 7 and 9, respectively.

Figures 4.51 and 4.52 show the result of CHClBr_2 formation in phase D as a function of time, and at six chlorine concentrations, for pH 7 and 9, respectively.

Figures 4.53 and 4.54 show the results of CHBr_3 formation in phase D as a function of time, and at six chlorine concentrations, for pH 7 and 9, respectively. It should be noted that the yield of CHBr_3 was much higher in experimental phase D relative to experimental phase A, B and C, due to addition 1×10^{-4} mol/L Br^- .

Examination of data reveals that the addition of 1×10^{-4} mol/L Br^- in ground water caused increase in yield of brominated THM's. Associated with this, a substantial reduction in CHCl_3 concentration was observed with increasing in amounts of CHCl_2Br , CHClBr_2 and CHBr_3 .

The relative concentration in mol/L observed in experimental phase D were:



Figures 4.55 and 4.56 show the results of THM formation on phase D as a function of time and at six chlorine concentrations, for pH 7 and 9, respectively. THM concentration increased with time, higher chlorine concentration and higher pH with the exception of chlorine concentration 4 which was the break point.

Figures 4.57 and 4.58 show the results of total organic Br in phase D as a function of time, and at six chlorine concentrations, for

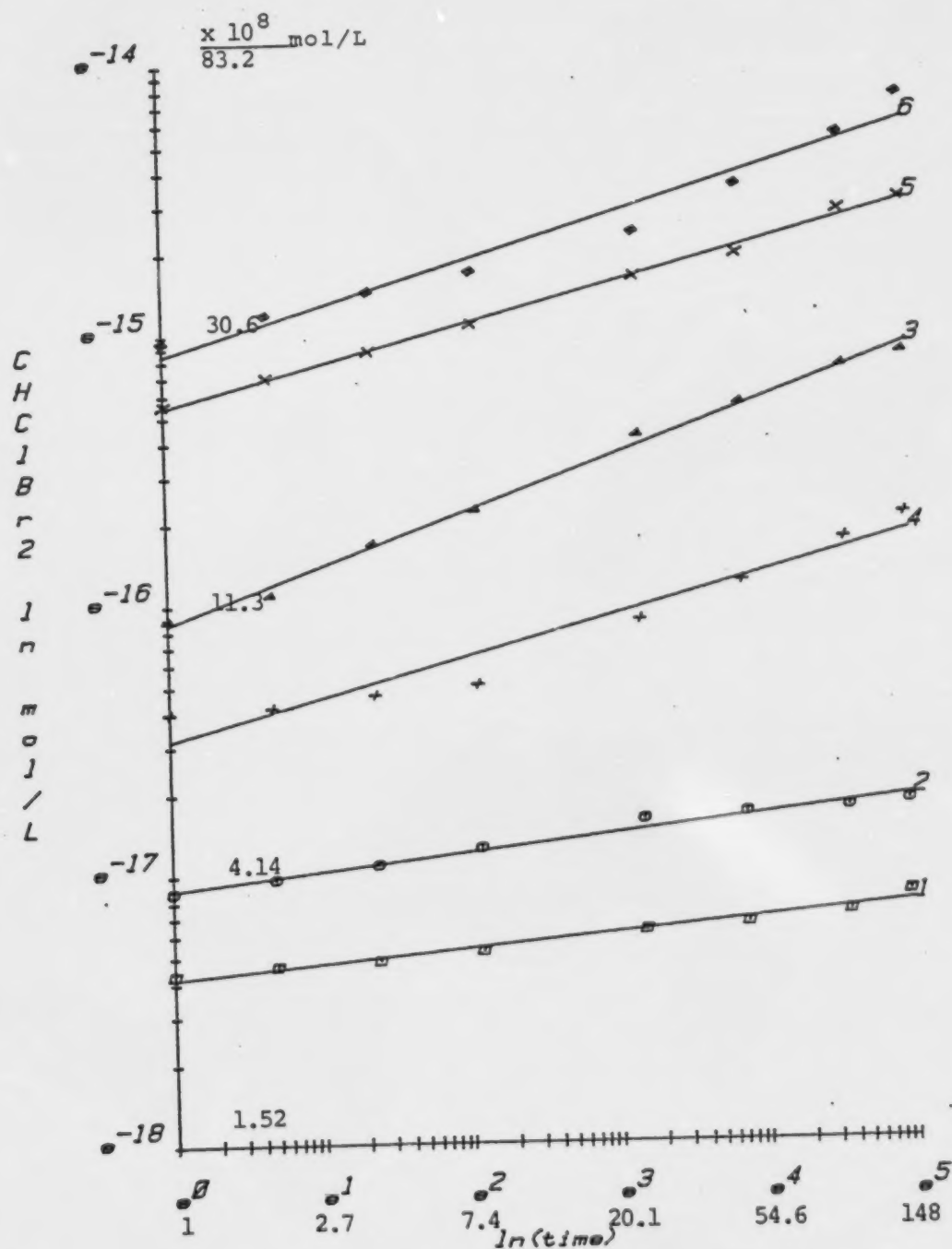


Fig. 4.51. CHClBr_2 formation as a function of time at six chlorine concentrations (Phase D, $1 \times 10^{-4} \text{ mol/L}$ Bromide, pH 7).
(Time in hours.)

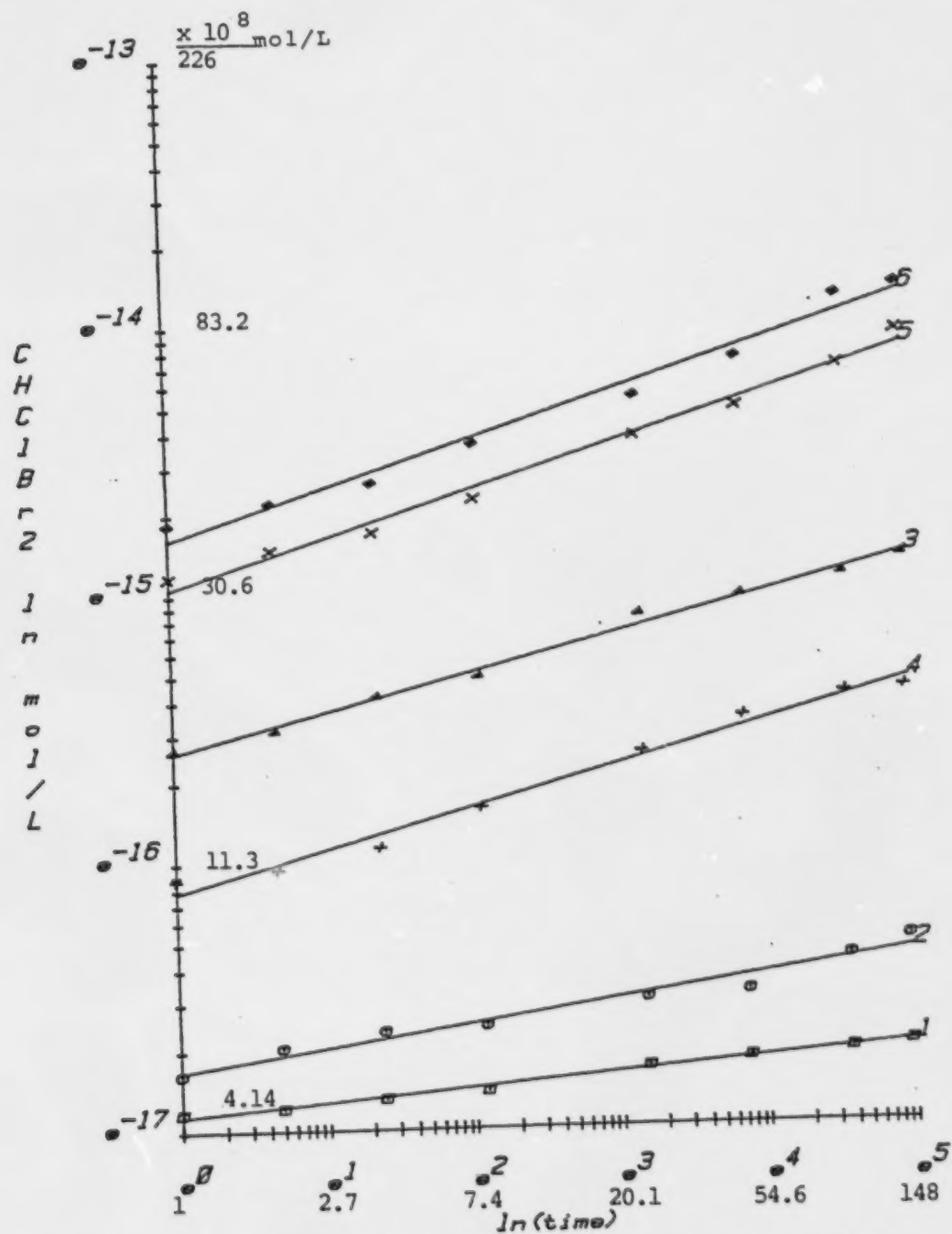


Fig. 4.52 CHClBr_2 formation as a function of time at six chlorine concentrations (Phase D, 1×10^{-4} mol/L Bromide, pH 9). (Time in hours.)

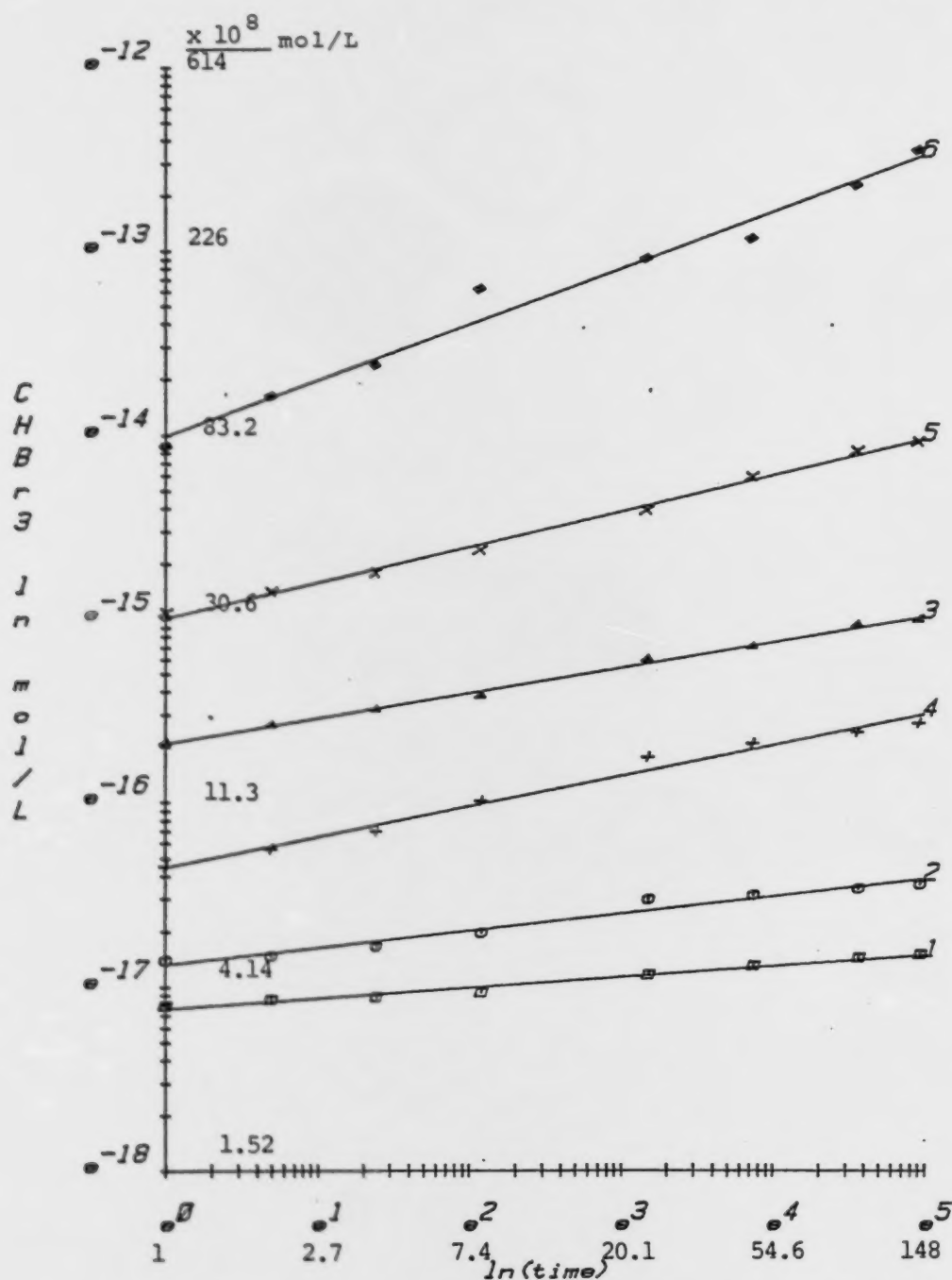


Fig. 4.53. CHBr_3 formation as a function of time at six chlorine concentration (Phase D, 1×10^{-4} mol/L Bromide, pH 7). (Time in hours.)

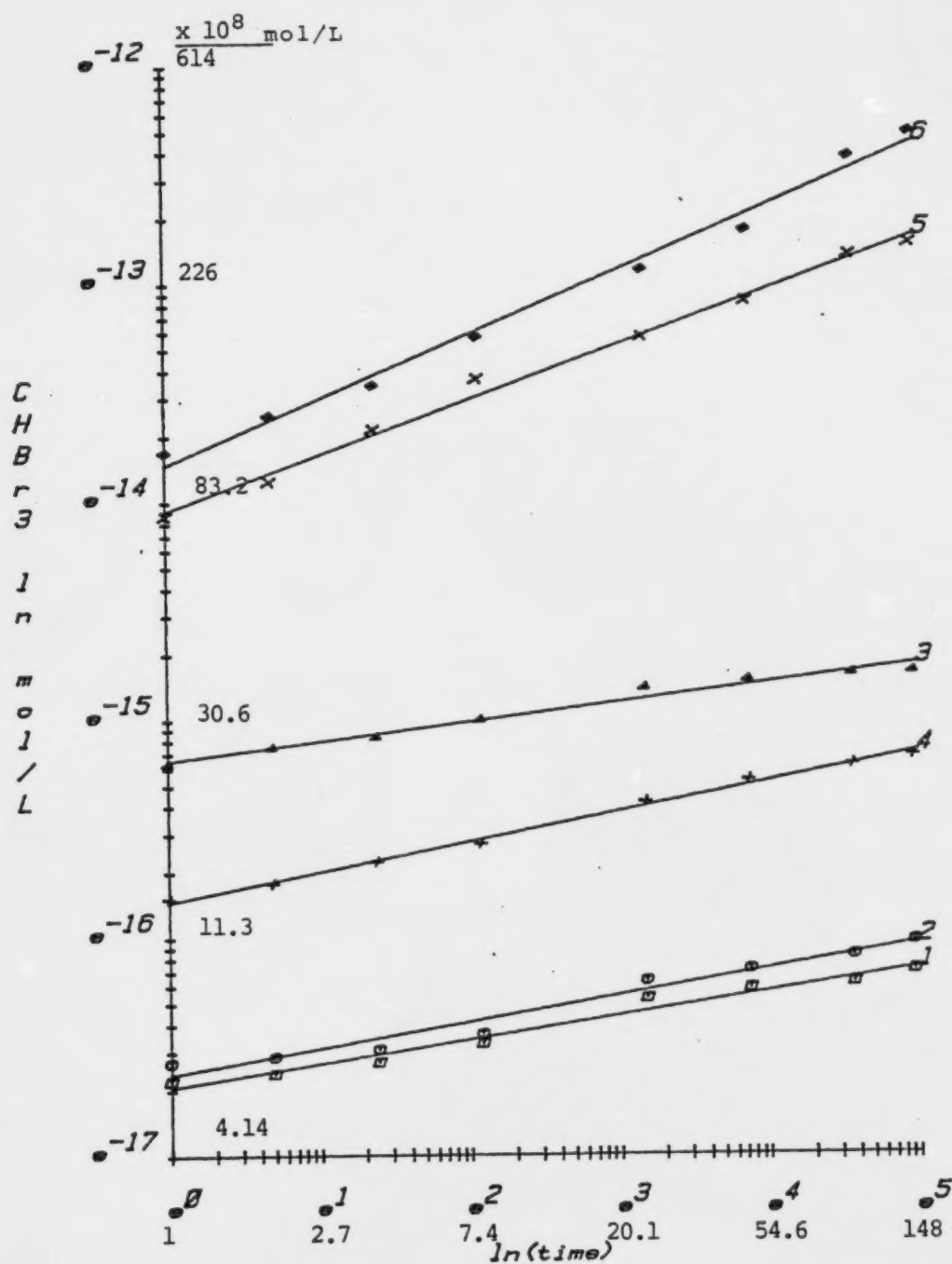


Fig. 4.54. CHBr_3 formation as a function of time at six chlorine concentration (Phase D, 1×10^{-4} mol/L Bromide, pH 9).

(Time in hours.)

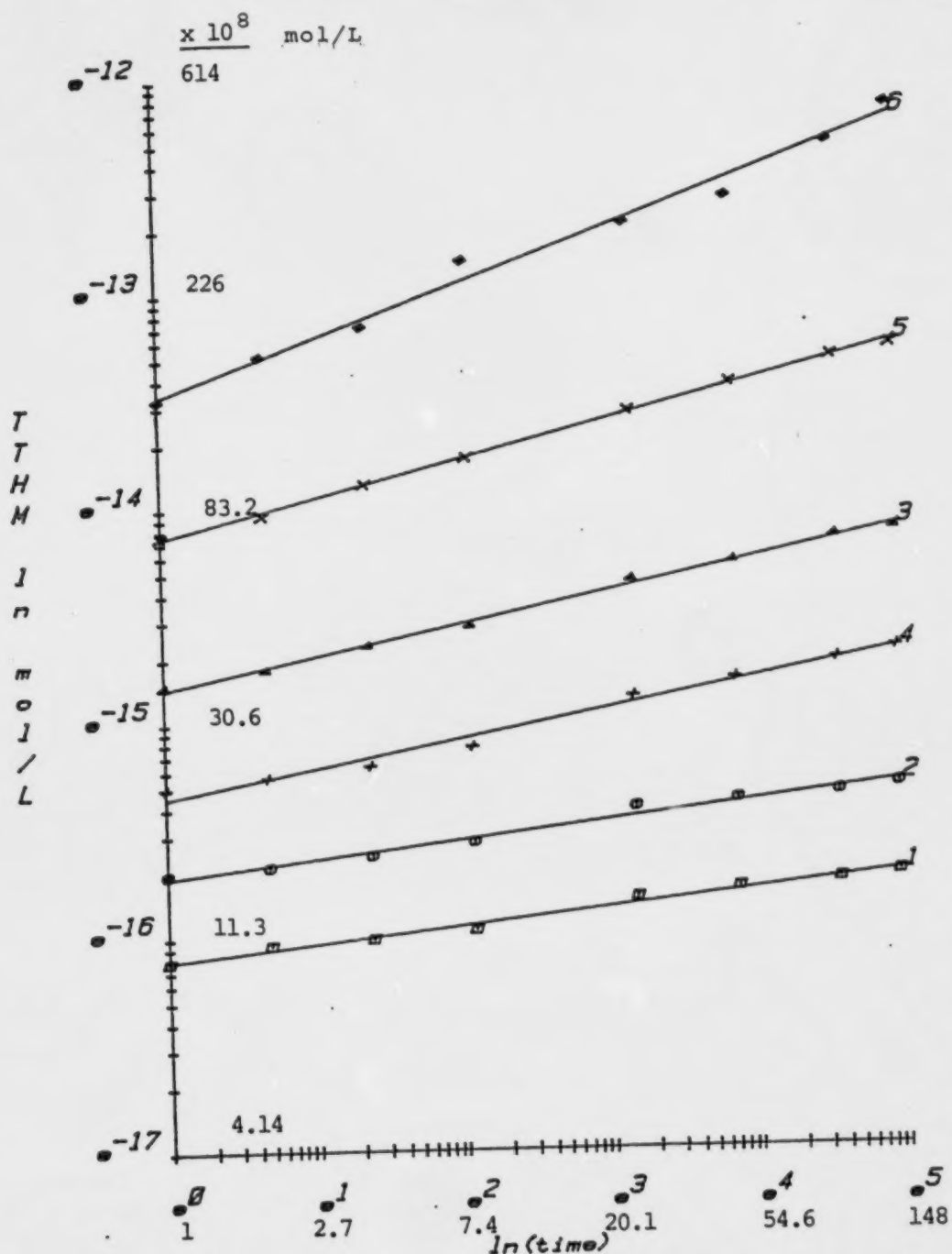


Fig. 4.55. THM formation as a function of time at six chlorine concentration (Phase D, 1×10^{-4} mol/L Bromide, pH 7). (Time in hours.)

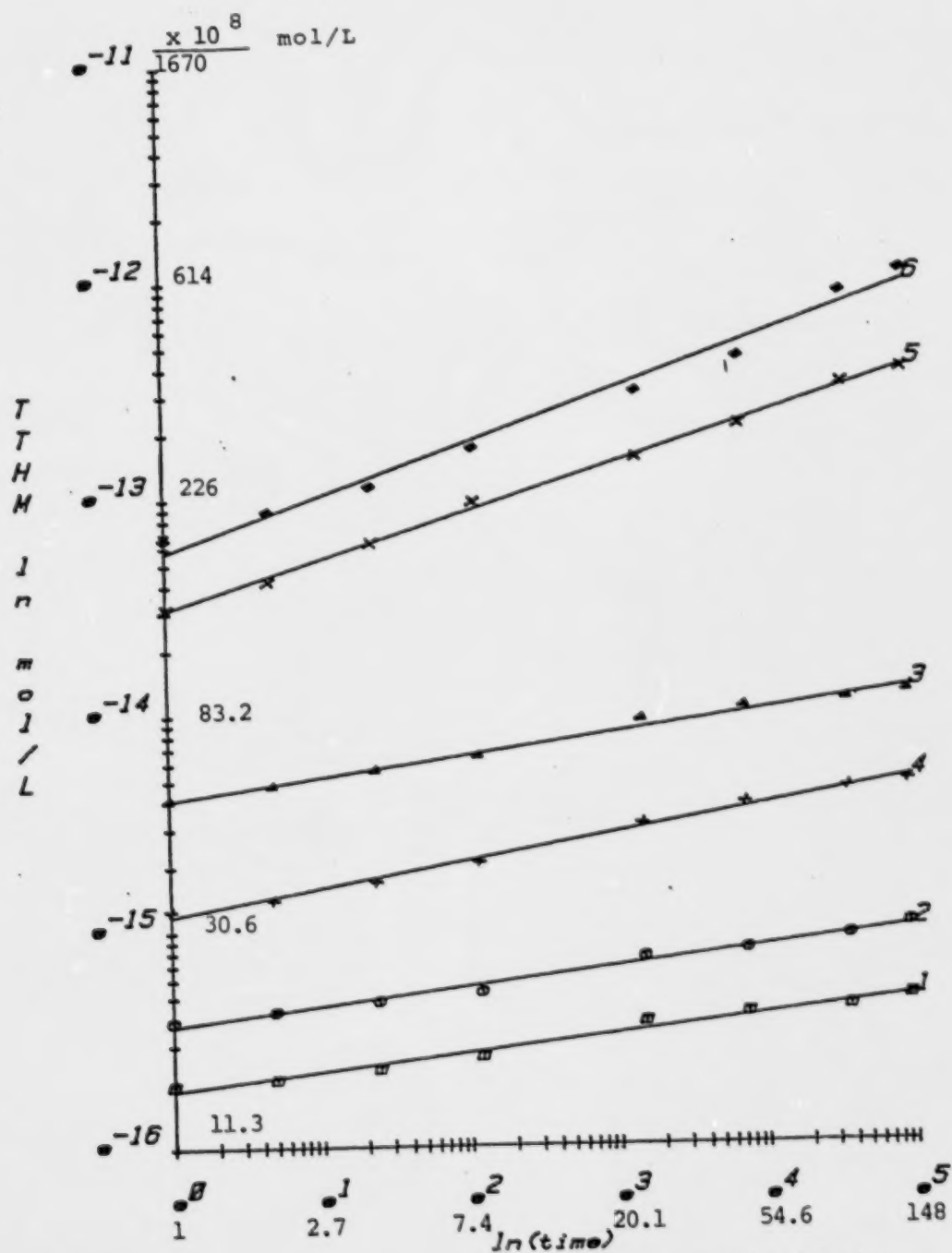


Fig. 4.56. TTHM formation as a function of time at six chlorine concentration (Phase D, 1×10^{-4} mol/L Bromide, pH 9).
(Time in hours.)

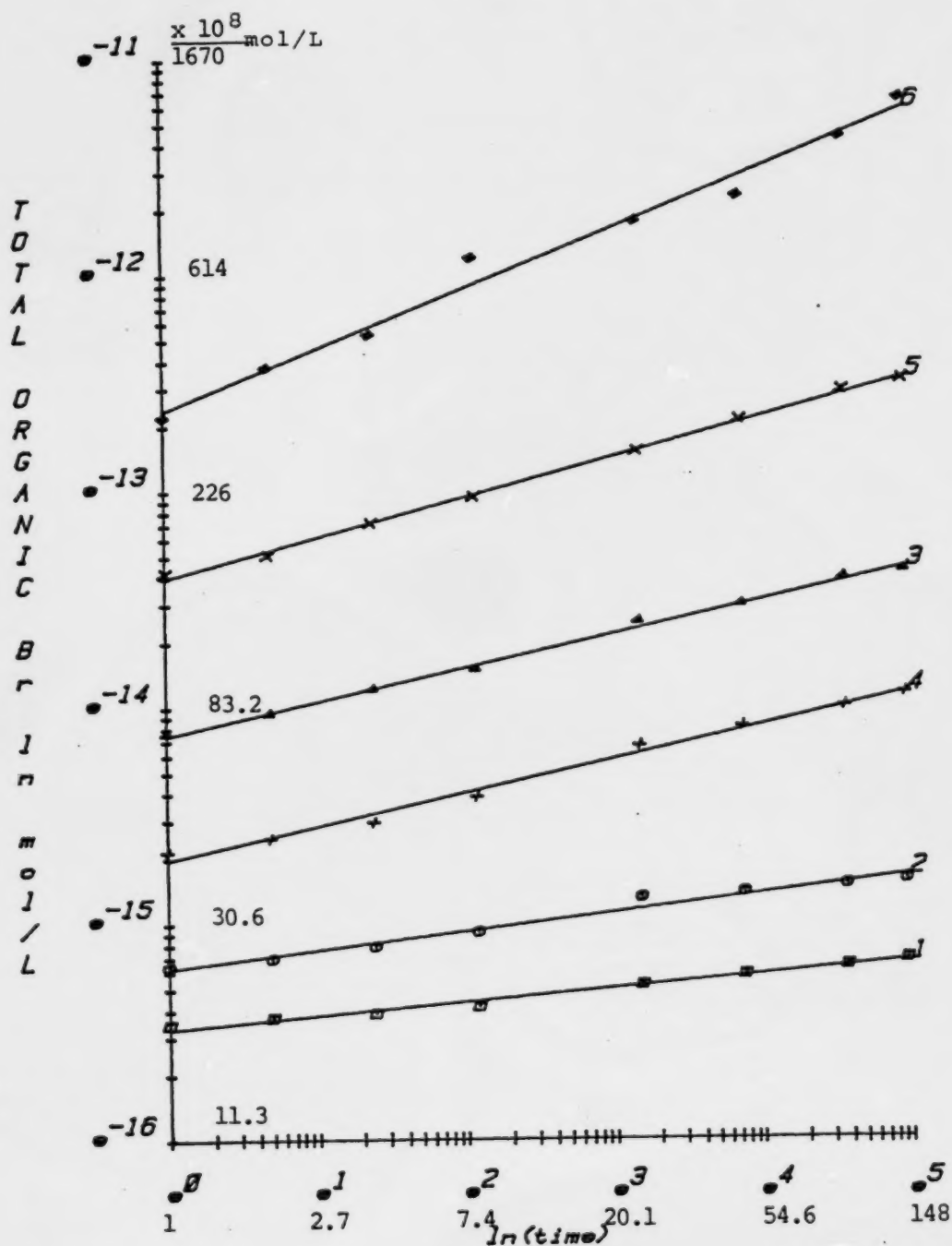


Fig. 4.57. Total organic Br formation as a function of time at six chlorine concentration (Phase D, 1×10^{-4} mol/L Bromide, pH 7).

(Time in hours.)

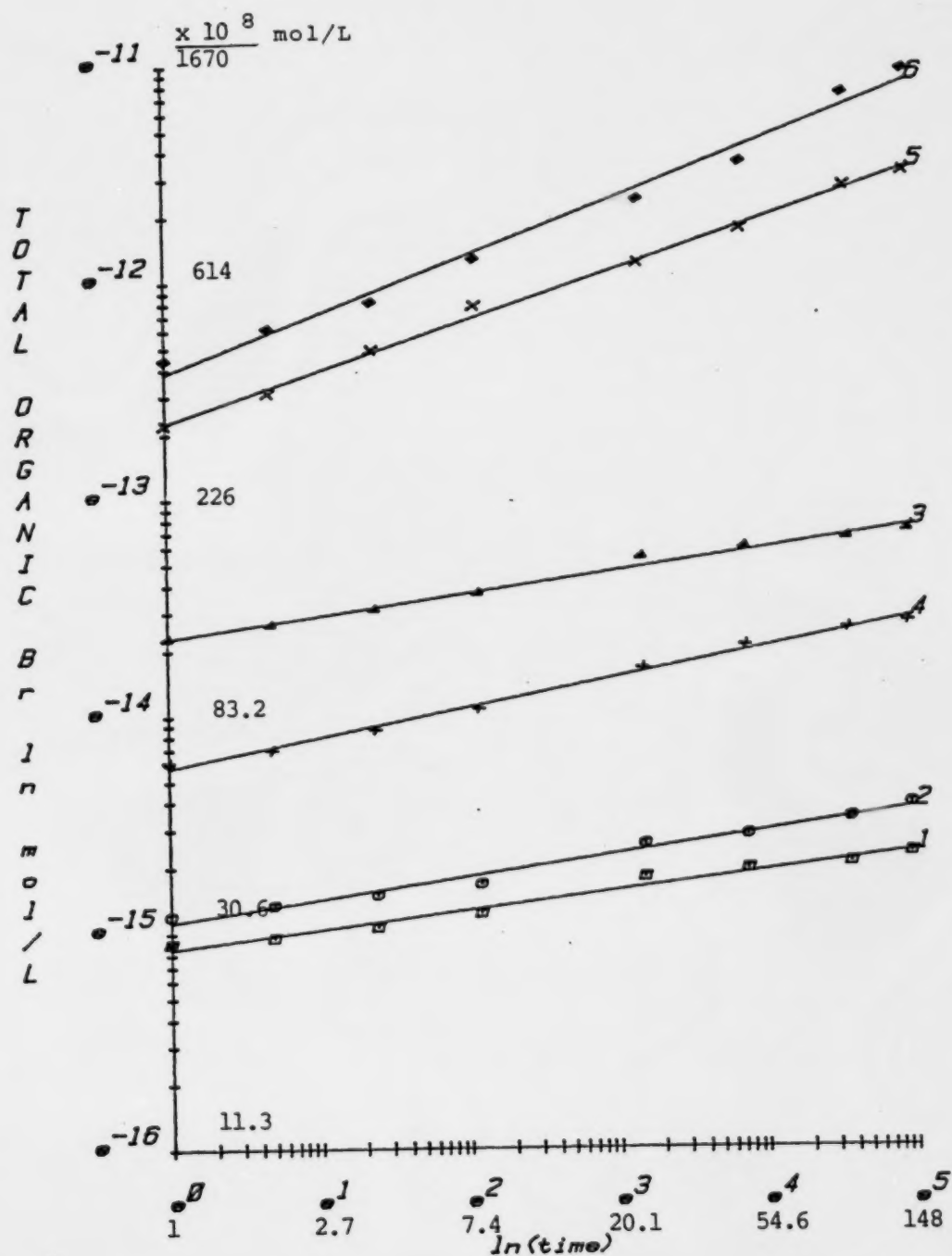


Fig. 4.58. Total organic Br formation as a function of time at six chlorine concentration (Phase D, 1×10^{-4} mol/L Bromide, pH 9).

(Time in hours.)

pH 7 and 9, respectively. The concentration of total organic Br was significantly higher relative to phase A, B and C, due to the addition of 1×10^{-4} mol/L Br^- to the sample of groundwater. The concentration of total organic Br at 144 hours reaction time was below 1930×10^{-9} mol/L in chlorine concentrations 1, 2, 3 and 4 at both pH 7 and 9. At chlorine concentration 5 the total organic Br was 3740×10^{-9} mol/L at pH 7 and 10100×10^{-9} mol/L at pH 9 after 144 hours reaction time. At chlorine concentration 6 the concentration was 5260×10^{-9} mol/L at pH 7 and 13700×10^{-9} mol/L at pH 9 after 144 hours reaction time.

Figures 4.59 and 4.60 show the result of total Cl in phase D as a function of time and at six chlorine concentrations, for pH 7 and 9, respectively. The concentration at 144 hours reaction time was below 779×10^{-9} mol/L in chlorine concentrations 1, 2, 3 and 4 at both pH 7 and 9. At chlorine concentration 5 the total organic Cl was 1410×10^{-9} mol/L at pH 7 and 1960×10^{-9} mol/L at pH 9 after 144 hours reaction time. At chlorine concentration 6 the concentration was 2100×10^{-9} mol/L at pH 7 and 2870×10^{-9} mol/L at pH 9 after 144 hours reaction time.

The mole ratio of total organic Cl to Br fluctuated differently throughout the eight reaction times in experimental phase D. Table 4.21 presents the mole ratio of total organic Cl/Br throughout the eight reaction times in experimental phase D.

The mole percent of incorporated was calculated based on the addition of 1×10^{-4} mol/L Br^- to groundwater. In general, as expected, the incorporated percentage of Br increased due to higher

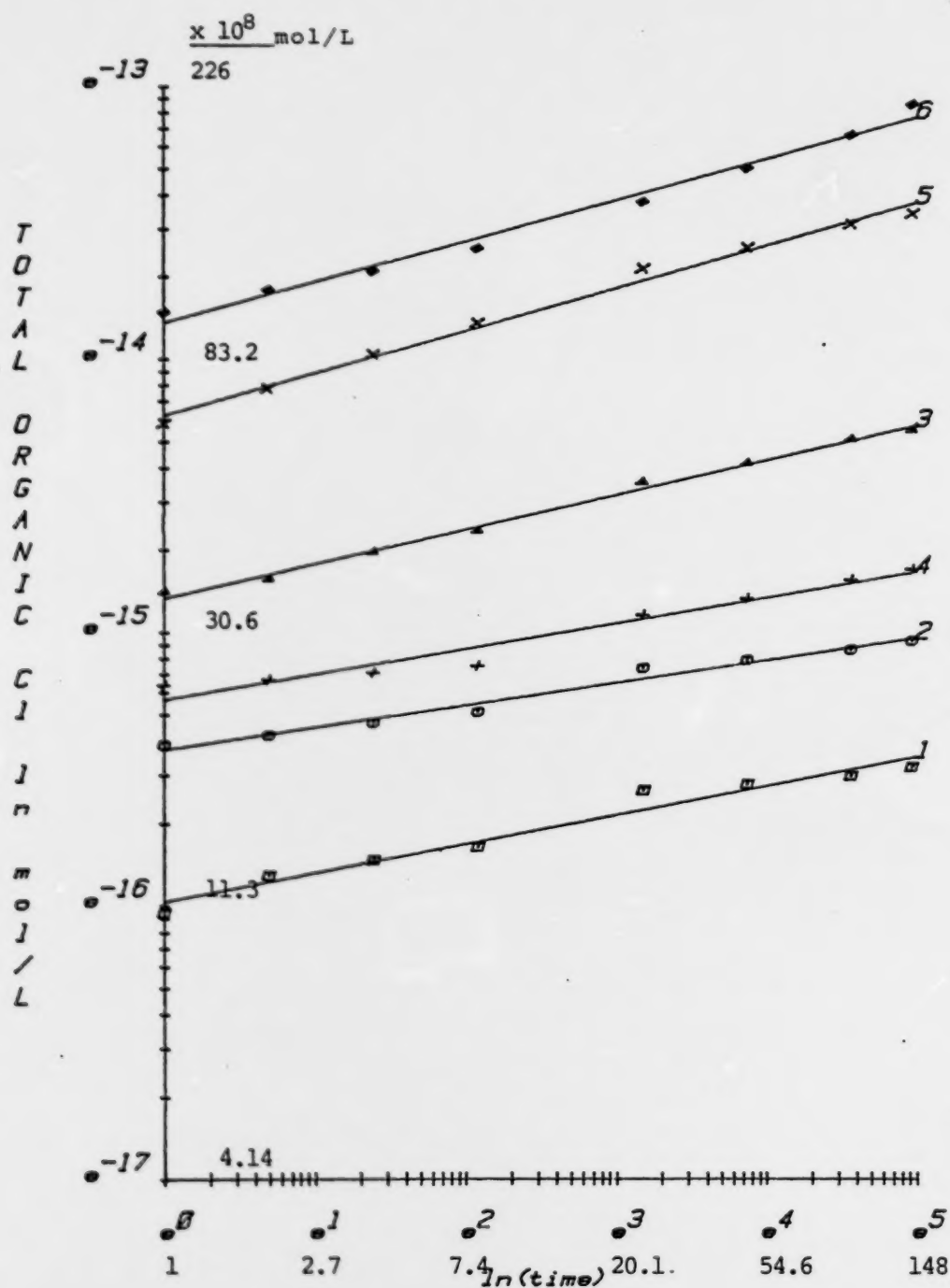


Fig. 4.59. Total organic Cl formation as a function of time at six chlorine concentration (Phase D, 1×10^{-4} mol/L Bromide, pH 7)..
(Time in hours.)

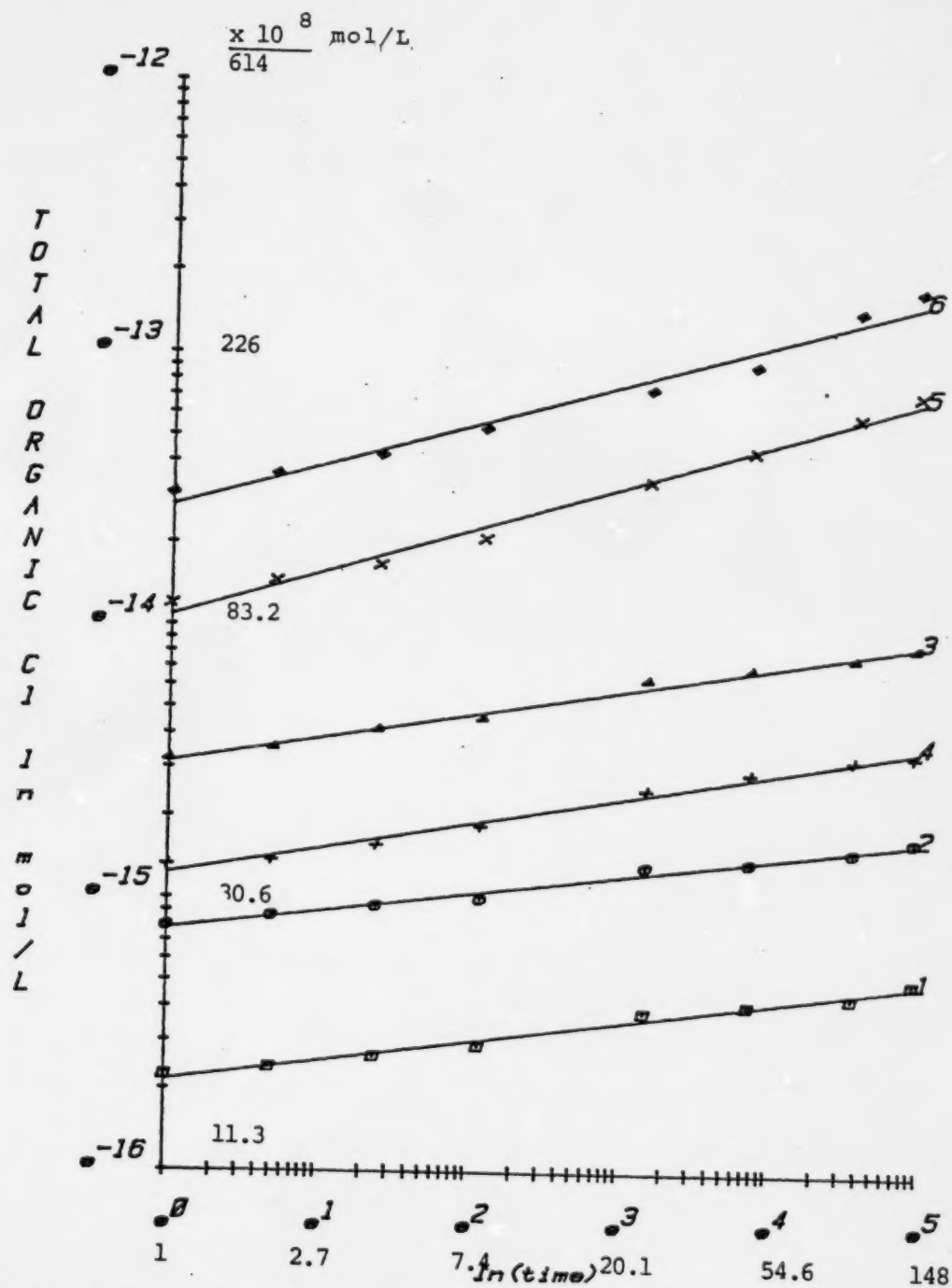


Fig. 4.60. Total organic Cl formation as a function of time at six chlorine concentration (Phase D, 1×10^{-4} mol/L Bromide, pH 9).
(Time in hours.)

TABLE 4.21

THE MOLE RATIO OF ORGANIC Cl/Br THROUGHOUT
EIGHT REACTION TIMES (HOURS) IN EXPERIMENTAL PHASE D.

Chlorine Concentration Number	pH	Range
1	7	0.570 - 0.748
	9	0.511 - 0.550
2	7	0.776 - 0.806
	9	0.699 - 0.831
3	7	0.414 - 0.480
	9	0.398 - 0.427
4	7	0.438 - 0.589
	9	0.413 - 0.512
5	7	0.377 - 0.442
	9	0.191 - 0.281
6	7	0.153 - 0.308
	9	0.178 - 0.313

chlorine concentration, the addition of 1×10^{-4} mol/L Br^- to groundwater and higher pH. Table 4.22 presents the mole percent Br incorporated of Br at minimum (one) and maximum (144) hour reaction times in experimental phase D.

In general, as expected, the mole percent Cl incorporated increased due to higher chlorine concentrations and pH with the exception of chlorine concentration 4 which was at the breakpoint. Table 4.23 presents the mole percent Cl at minimum (one) and maximum (144) hours reaction time in experimental phase D.

D. Effect of Bromide on Formation and Distribution of THM's:

The importance of the effect of bromide on the formation of trihalomethanes during chlorination of groundwater was studied by the addition of three concentrations of bromide (1×10^{-6} , 1×10^{-5} mol/L and 1×10^{-4} mol/L) to groundwater prior to chlorination. As stated previously experimental design was divided into four phases with the bromide concentration being the determining factor. In experimental phase A no bromide was added to the groundwater. In experimental phase B, 1×10^{-6} mol/L bromide, experimental phase C, 1×10^{-5} mol/L bromide and experimental phase D, 1×10^{-4} mol/L bromide was added to the groundwater. The impact of bromide concentration on the formation and distribution of CHCl_3 , CHCl_2Br , CHClBr_2 , CHBr_3 and TTHM was investigated as a function of time, pH, and Chlorine concentration.

Chloroform. The effect of 1×10^{-6} mol/L bromide on the concentration of CHCl_3 in experimental phase B is summarized in

TABLE 4.22

THE MOLE PERCENT Br INCORPORATED AT MINIMUM (1)
AND MAXIMUM (144) HOURS REACTION TIME IN EXPERIMENTAL
PHASE D.

Chlorine Concentration Number	pH	Reaction Time (hours)	
		1	144
1	7	0.193	0.258
	9	0.292	0.437
2	7	0.252	0.371
	9	0.332	0.548
3	7	0.740	1.55
	9	1.19	1.93
4	7	0.428	0.880
	9	0.674	1.27
5	7	1.56	3.74
	9	3.20	10.1
6	7	3.20	13.7
	9	4.31	16.1

TABLE 4.23

THE MOLE PERCENT Cl INCORPORATED OF Cl AT MINIMUM (1)
AND MAXIMUM (144) HOUR REACTION TIME IN EXPERIMENTAL
PHASE D.

Chlorine Concentration Number	pH	Reaction Time (hours)	
		1	144
1	7	0.390	0.663
	9	0.567	0.809
2	7	0.180	0.263
	9	0.244	0.339
3	7	0.210	0.380
	9	0.301	0.461
4	7	0.112	0.170
	9	0.153	0.232
5	7	0.203	0.435
	9	0.277	0.605
6	7	0.200	0.425
	9	0.273	0.581

Table 4.24. the results are expressed as the percentage of CHCl_3 formed in chlorinated groundwater with 1×10^{-6} mol/L bromide added (experimental phase B), as compared to ground water with no bromide added (experimental phase A), at pH 7 and 9, at eight reaction times (hours), and at six chlorine concentrations.

In general, the addition of 1×10^{-6} mol/L Br^- had a very small effect on the distribution of THM's and CHCl_3 remained the predominant compound in distribution of THM's.

The effect of 1×10^{-5} mol/L bromide on the relative CHCl_3 concentration in experimental phase C is shown in Table 4.25. The results are presented as the percentage of CHCl_3 formed in chlorinated groundwater with 1×10^{-5} mol/L bromide added (experimental phase C), as compared to groundwater with no bromide added (experimental phase A), at pH 7 and 9, at eight reaction times (hours), and at six chlorine concentrations. It should be noted that in experimental phase C, CHCl_3 was the predominant trihalomethane formed at chlorine concentrations 1, 2, 3 and 4, but, at chlorine concentrations 5 and 6 this predominance shifted. In general it was shown that at or before break point the chloroform concentration increased relative to phase A. After the break point the CHCl_3 concentration decreased relative to phase A. A detailed explanation of this phenomena is not available at this time.

The effect of 1×10^{-4} mol/L bromide on the relative CHCl_3 concentration in experimental phase D is shown in Table 4.26. The results are presented as a percentage of CHCl_3 formed in chlorinated groundwater with 1×10^{-4} mol/L Br^- added (experimental phase

TABLE 4.24

THE PERCENTAGE OF CHCl_3 FORMED IN CHLORINATED GROUND WATER WITH 1×10^{-6} mol/L BROMIDE ADDED (EXPERIMENTAL PHASE B) AS COMPARED TO GROUNDWATER WITH NO BROMIDE ADDED (EXPERIMENTAL PHASE A), AT pH 7 AND 9, AT EIGHT REACTION TIMES (HOURS), AND AT SIX CHLORINE CONCENTRATIONS.

Chlorine Concentration Number	pH	Reaction Time (hours)							
		1	2	4	8	24	48	96	144
1	7	-45.5	-45.8	-41.4	-37.5	-28.9	-21.1	-11.6	-8.00
	9	-7.27	-7.05	-5.91	+0.22	+11.8	+35.8	+48.0	+48.5
2	7	+39.8	+36.7	+31.9	+28.0	+28.1	+18.4	+19.8	+22.9
	9	+56.2	+72.4	+37.3	+27.8	+20.7	+21.6	+19.6	+16.7
3	7	+38.0	+53.7	+44.5	+43.6	+44.9	+37.6	+33.9	+21.2
	9	+238	+223	+183	+193	+156	+147	+135	+128
4	7	+216	+194	+167	+143	+149	+132	+135	+161
	9	+380	+303	+272	+246	+223	+208	+189	+163
5	7	-4.67	-9.44	-24.7	-2.25	+41.0	+75.3	+93.3	+108
	9	+3.22	+4.41	+1.11	+8.98	+50.5	+112	+145	+166
6	7	-12.4	-10.4	-8.86	-16.5	+20.0	+34.3	+2.68	+2.67
	9	+29.7	+13.2	+12.2	+10.0	+21.9	+31.9	+26.6	+12.5

TABLE 4.25

THE PERCENTAGE OF CHCl_3 FORMED IN CHLORINATED GROUND WATER WITH 1×10^{-5} mol/L BROMIDE ADDED (EXPERIMENTAL PHASE C) AS COMPARED TO GROUNDWATER WITH NO BROMIDE ADDED (EXPERIMENTAL PHASE A), AT pH 7 AND 9, AT EIGHT REACTION TIMES (HOURS), AND AT SIX CHLORINE CONCENTRATIONS.

Chlorine Concentration Number	pH	Reaction Time (hours)							
		1	2	4	8	24	48	96	144
1	7	-14.5	-11.6	-8.64	-3.41	+0.68	+10.7	+14.4	+15.8
	9	-8.86	-7.05	-3.41	-1.33	+10.0	+41.3	+32.8	+31.9
2	7	+18.6	+40.2	+24.0	+21.2	+20.6	+13.0	+13.0	+22.0
	9	+54.4	+68.3	+32.3	+21.3	+20.9	+20.6	+15.6	+13.7
3	7	+152	+154	+143	+141	+153	+142	+137	+148
	9	+201	+187	+161	+181	+150	+155	+140	+123
4	7	+449	+439	+426	+390	+399	+387	+381	+352
	9	+516	+417	+394	+385	+381	+375	+348	+336
5	7	-10.9	-20.7	-42.7	-41.1	-38.0	-29.1	-22.3	-20.7
	9	-24.6	-26.8	-33.2	-31.9	-29.1	-22.9	-18.5	-7.50
6	7	-23.0	-26.6	-32.8	-43.4	-34.2	-30.4	-51.8	-53.1
	9	-20.1	-29.5	-33.2	-40.7	-43.6	-40.5	-43.2	-47.0

TABLE 4.26

THE PERCENTAGE OF CHCl_3 FORMED IN CHLORINATED GROUND WATER WITH 1×10^{-4} mol/L BROMIDE ADDED (EXPERIMENTAL PHASE D) AS COMPARED TO GROUNDWATER WITH NO BROMIDE ADDED (EXPERIMENTAL PHASE A), AT pH 7 AND 9, AT EIGHT REACTION TIMES (HOURS), AND AT SIX CHLORINE CONCENTRATIONS.

Chlorine Concentration Number	pH	Reaction Time (hours)							
		1	2	4	8	24	48	96	144
1	7	-66.4	-54.7	-51.8	-47.5	-29.8	-30.0	-28.7	-27.1
	9	-43.6	-42.0	-40.2	-38.0	-28.9	-26.2	-22.4	-17.4
2	7	-7.50	-8.90	-11.0	-13.9	-0.19	-9.51	-9.68	-8.00
	9	+32.2	+33.0	+2.67	-7.50	-2.97	-3.33	-4.00	-5.00
3	7	-56.9	-56.5	-57.7	-59.1	-54.5	-56.9	-57.6	-62.2
	9	-45.5	-48.9	-53.1	-51.8	-54.5	-56.3	-59.8	-62.1
4	7	-18.1	-23.9	-40.0	-39.1	-29.1	-34.8	-37.3	-41.3
	9	+1.63	-7.40	-14.8	-21.1	-15.3	-21.8	-24.8	-29.1
5	7	-86.0	-87.6	-90.9	-90.7	-89.7	-89.6	-89.7	-89.8
	9	-86.8	-87.9	-89.6	-89.8	-89.0	-88.6	-88.0	-87.7
6	7	-87.5	-89.3	-90.7	-92.3	-92.7	-92.4	-95.0	-95.5
	9	-86.8	-88.7	-90.0	-91.4	-92.8	-93.5	-94.4	-95.2

D), as compared to groundwater with no bromide added (experimental phase A), at pH 7 and 9, at eight reaction times (hours), and at six chlorine concentrations. In experimental phase D with few exceptions the relative concentration of CHCl_3 was lower than in phase A. It should be noted that the addition of 1×10^{-4} mol/L Br^- to groundwater caused a substantial reduction in CHCl_3 with an increased amount of the brominated compounds.

Bromodichloromethane: The effect of 1×10^{-6} mol/L bromide ion on the concentration of CHCl_2Br was studied in experimental phase B and is shown in Table 4.27. The results are presented as the percentage of CHCl_2Br formed in chlorinated groundwater with 1×10^{-6} mol/L bromide added (experimental phase B), as compared to groundwater with no bromide added (experimental phase A), at pH 7 and 9, at eight reaction times (hours), and at six chlorine concentrations.

The effect of 1×10^{-5} mol/L bromide ion on the concentration of CHCl_2Br in experimental phase C is shown in Table 4.28. The results are presented as a percentage of CHCl_2Br formed in chlorinated groundwater with 1×10^{-5} mol/L bromide added (experimental phase C), as compared to ground water with no bromide added (experimental phase A), at pH 7 and 9, at eight reaction times (hours), and at six chlorine concentration.

The effect of 1×10^{-4} mol/L bromide ion on the concentration of CHCl_2Br was studied in experimental phase D as is shown in Table 4.29. The results are presented as percentages of CHCl_2Br formed in chlorinated groundwater with 1×10^{-4} mol/L bromide added (experimental

TABLE 4.27

THE PERCENTAGE OF CHCl_2Br FORMED IN CHLORINATED GROUND WATER WITH 1×10^{-6} mol/L BROMIDE ADDED (EXPERIMENTAL PHASE B) AS COMPARED TO GROUNDWATER WITH NO BROMIDE ADDED (EXPERIMENTAL PHASE A), AT pH 7 AND 9, AT EIGHT REACTION TIMES (HOURS), AND AT SIX CHLORINE CONCENTRATIONS.

Chlorine Concentration Number	pH	Reaction Time (hours)							
		1	2	4	8	24	48	96	144
1	7	-8.10	-7.62	-9.55	-6.52	-8.80	-2.00	+2.30	+6.67
	9	+73.2	+77.7	+80.9	+82.3	+48.2	+53.9	+75.4	+77.9
2	7	+91.7	+86.4	+91.2	+102	+98.2	+107	+107	+102
	9	+97.7	+83.4	+75.5	+81.9	+86.3	+99.7	+77.6	+112
3	7	+393	+361	+351	+345	+327	+337	+351	+387
	9	+473	+413	+434	+436	+435	+449	+402	+435
4	7	+373	+357	+366	+361	+352	+347	+345	+324
	9	+504	+512	+532	+531	+548	+456	+411	+318
5	7	+22.1	+23.6	+22.1	+28.5	+31.7	+44.6	+34.1	+40.6
	9	+26.1	+39.4	+35.5	+12.7	+39.3	+67.0	+82.3	+111
6	7	-32.2	-43.0	-31.8	-30.5	-6.34	+2.53	+8.76	+6.60
	9	-19.2	-7.21	-2.78	+7.05	+31.0	+24.7	+31.8	+22.3

TABLE 4.28

THE PERCENTAGE OF CHCl_2Br FORMED IN CHLORINATED GROUND WATER WITH 1×10^{-5} mol/L BROMIDE ADDED (EXPERIMENTAL PHASE C) AS COMPARED TO GROUNDWATER WITH NO BROMIDE ADDED (EXPERIMENTAL PHASE A), AT pH 7 AND 9, AT EIGHT REACTION TIMES (HOURS), AND AT SIX CHLORINE CONCENTRATIONS.

Chlorine Concentration Number	pH	Reaction Time (hours)							
		1	2	4	8	24	48	96	144
1	7	+73.8	+76.7	+79.5	+79.1	+73.2	+82.0	+90.4	+84.4
	9	+82.7	+88.2	+91.8	+95.9	+76.8	+78.9	+83.6	+85.4
2	7	+102	+98.0	+104	+99.2	+90.4	+87.6	+80.0	+70.0
	9	+98.8	+90.0	+88.4	+93.2	+94.1	+98.1	+99.4	+119
3	7	+503	+455	+437	+408	+439	+479	+487	+502
	9	+581	+526	+582	+600	+628	+712	+604	+608
4	7	+565	+536	+528	+494	+473	+515	+503	+498
	9	+692	+772	+816	+835	+904	+817	+775	+651
5	7	+60.4	+48.2	+41.4	+25.1	+45.8	+40.8	+55.7	+55.3
	9	+44.6	+38.8	+30.3	+5.27	+53.2	+58.8	+75.8	+88.9
6	7	+11.2	-7.80	+0.70	-0.63	+17.0	+32.5	+59.6	+53.8
	9	-2.38	+0.44	+6.81	+2.56	+28.6	+55.3	+87.5	+75.7

TABLE 4.29

THE PERCENTAGE OF CHCl_2Br FORMED IN CHLORINATED GROUND WATER WITH 1×10^{-4} mol/L BROMIDE ADDED (EXPERIMENTAL PHASE D) AS COMPARED TO GROUNDWATER WITH NO BROMIDE ADDED (EXPERIMENTAL PHASE A), AT pH 7 AND 9, AT EIGHT REACTION TIMES (HOURS), AND AT SIX CHLORINE CONCENTRATIONS.

Chlorine Concentration Number	pH	Reaction Time (hours)							
		1	2	4	8	24	48	96	144
1	7	+78.6	+85.7	+82.3	+81.7	+99.6	+105	+105	+101
	9	+99.1	+109	+122	+126	+107	+113	+115	+119
2	7	+109	+109	+127	+130	+150	+147	+140	+133
	9	+140	+118	+122	+132	+153	+161	+159	+166
3	7	+218	+199	+191	+184	+188	+184	+187	+187
	9	+339	+300	+313	+312	+333	+337	+266	+262
4	7	+138	+123	+122	+116	+137	+135	+114	+95.2
	9	+272	+282	+304	+300	+322	+272	+247	+187
5	7	-10.4	-7.50	-7.35	-10.2	-9.42	-13.2	-14.6	-14.6
	9	+10.4	+4.69	-4.21	-26.7	-8.04	+4.91	+10.0	+14.6
6	7	-13.4	-40.0	-31.7	-32.2	-20.7	-12.9	-10.6	-16.1
	9	-5.56	-5.29	-2.92	-1.79	+4.52	+12.0	+34.1	+27.2

phase D), as compared to groundwater with no bromide added (experimental phase A), at pH 7 and 9, at eight reaction times (hours), and at six chlorine concentration. In experimental phase D the percentage increase of CHCl_2Br concentration was much higher at chlorine concentration 1, 2, 3, and 4 relative to 5 and 6.

Chlorodibromomethane: The effect of 1×10^{-6} mol/L of bromide ion on the concentration of CHClBr_2 in experimental phase B. is presented in Table 4.30. The results are presented as the percentage of CHClBr_2 formed in chlorinated ground water with 1×10^{-6} mol/L bromide added (experimental phase B), as compared to groundwater with no bromide added (experimental phase A), at pH 7 and 9, at eight reaction times (hours), and at six chlorine concentrations.

The effect of 1×10^{-5} mol/L bromide ion on the concentration of CHClBr_2 in experimental phase C is presented in Table 4.31. The results are presented as the percentage of CHClBr_2 formed in chlorinated groundwater with 1×10^{-5} mol/L bromide added (experimental phase C) as compared to ground water with no bromide added (experimental phase A), at pH 7 and 9, at eight reaction times, and at six chlorine concentrations.

The effect of 1×10^{-4} mol/L bromide ion on the concentration of CHClBr_2 an experimental phase D is presented in Table 4.32. The results are presented as the percentage of CHClBr_2 formed in chlorinated groundwater with 1×10^{-4} mol/L bromide added (experimental phase D) as compared to groundwater with no bromide added (experimental phase A), at pH 7 and 9, at eight reaction times

TABLE 4.30

THE PERCENTAGE OF CHClBr_2 FORMED IN CHLORINATED GROUND WATER WITH 1×10^{-6} mol/L BROMIDE ADDED (EXPERIMENTAL PHASE B) AS COMPARED TO GROUNDWATER WITH NO BROMIDE ADDED (EXPERIMENTAL PHASE A), AT pH 7 AND 9, AT EIGHT REACTION TIMES (HOURS), AND AT SIX CHLORINE CONCENTRATIONS.

Chlorine Concentration Number	pH	Reaction Time (hours)							
		1	2	4	8	24	48	96	144
1	7	-8.33	-7.22	-8.10	-8.26	+6.52	+7.92	+10.0	+3.08
	9	+39.4	+40.0	+32.5	+29.0	+26.8	+29.5	+22.1	+14.6
2	7	+5.50	+8.18	+4.58	+12.4	+15.0	+15.6	+14.6	+18.3
	9	+22.7	+11.7	+7.45	+19.0	+24.7	+25.9	+24.5	+28.8
3	7	+68.4	+63.3	+70.0	+65.7	+69.5	+83.1	+106	+101
	9	+85.8	+88.2	+89.4	+89.4	+101	+104	+104	+111
4	7	+141	+137	+130	+118	+126	+123	+120	+110
	9	+157	+170	+163	+166	+165	+161	+150	+158
5	7	+29.1	+11.9	+9.78	+16.4	+13.2	+16.3	+25.8	+28.8
	9	+72.7	+8.40	-13.6	-14.3	+3.51	+23.2	+40.0	+49.6
6	7	+10.1	+10.4	-12.2	-8.10	+14.2	+5.51	+11.7	+17.8
	9	+40.0	+4.84	+1.94	-1.22	-1.56	+3.48	+5.32	+6.27

TABLE 4.31

THE PERCENTAGE OF CHClBr_2 FORMED IN CHLORINATED GROUND WATER WITH 1×10^{-5} mol/L BROMIDE ADDED (EXPERIMENTAL PHASE C) AS COMPARED TO GROUNDWATER WITH NO BROMIDE ADDED (EXPERIMENTAL PHASE A), AT pH 7 AND 9, AT EIGHT REACTION TIMES (HOURS), AND AT SIX CHLORINE CONCENTRATIONS.

Chlorine Concentration Number	pH	Reaction Time (hours)							
		1	2	4	8	24	48	96	144
1	7	+56.1	+60.1	+40.5	+36.5	+38.7	+34.2	+35.4	+26.2
	9	+67.2	+72.2	+59.5	+54.8	+56.4	+65.0	+57.1	+46.5
2	7	+32.5	+51.0	+17.1	+17.2	+19.2	+15.9	+13.9	+11.4
	9	+37.0	+32.5	+18.5	+19.9	+31.8	+35.0	+21.3	+27.0
	7	+96.8	+88.2	+89.4	+82.7	+87.1	+87.4	+87.3	+90.2
	9	+168	+172	+175	+197	+200	+211	+205	+213
	7	+154	+159	+147	+130	+135	+135	+138	+124
	9	+153	+166	+159	+162	+154	+153	+143	+148
5	7	+265	+252	+252	+120	+167	+187	+239	+273
	9	+306	+178	+124	+118	+224	+247	+271	+263
6	7	+228	+184	+201	+180	+258	+262	+319	+384
	9	+241	+165	+154	+140	+187	+228	+321	+324

TABLE 4.32

THE PERCENTAGE OF CHClBr_2 FORMED IN CHLORINATED GROUND WATER WITH 1×10^{-4} mol/L BROMIDE ADDED (EXPERIMENTAL PHASE D) AS COMPARED TO GROUNDWATER WITH NO BROMIDE ADDED (EXPERIMENTAL PHASE A), AT pH 7 AND 9, AT EIGHT REACTION TIMES (HOURS), AND AT SIX CHLORINE CONCENTRATIONS.

Chlorine Concentration Number	pH	Reaction Time (hours)							
		1	2	4	8	24	48	96	144
1	7	+234	+243	+198	+182	+203	+198	+209	+205
	9	+417	+424	+388	+375	+390	+404	+375	+346
2	7	+308	+288	+273	+280	+304	+296	+289	+283
	9	+365	+392	+361	+369	+394	+407	+465	+421
3	7	+619	+639	+768	+797	+1040	+1150	+1120	+1290
	9	+991	+1060	+1220	+1270	+1560	+1670	+1700	+1770
4	7	+618	+600	+572	+544	+715	+804	+914	+939
	9	+861	+896	+933	+2000	+1300	+1420	+1430	+1530
5	7	+269	+226	+166	+93.3	+110	+122	+157	+165
	9	+357	+202	+143	+144	+205	+229	+254	+257
6	7	+214	+174	+177	+150	+178	+186	+231	+269
	9	+280	+190	+168	+171	+191	+226	+300	+282

(hours), and at six chlorine concentrations.

Bromoform: The effect of 1×10^{-6} mol/L bromide ion on the concentration CHBr_3 in experimental phase B is shown in Table 4.33. The results are presented on the percentage of CHBr_3 formed in chlorinated groundwater with 1×10^{-6} mol/L bromide added (experimental phase B) as compared to groundwater with no bromide added (experimental phase A), at pH 7 and 9, at eight reaction time (hours), and at six chlorine concentrations.

The effect of 1×10^{-5} mol/L bromide ion on the concentration of CHBr_3 in experimental phase C is presented in Table 4.34. The results are presented as the percentage of CHBr_3 formed in chlorinated groundwater with 1×10^{-5} mol/L bromide added (experimental phase C), as compared to groundwater with no bromide added (experimental phase A), at pH 7 and 9, at eight reaction time (hours), and at six chlorine concentrations.

The concentration of CHBr_3 increased at all six chlorine concentration throughout eight reaction times, but, the percentage increase of CHBr_3 was much higher at chlorine concentration 5 and 6.

The effect of 1×10^{-4} mol/L bromide ion on the concentration of CHBr_3 in experimental phase D is shown in Table 4.35. The results are presented as the percentage of CHBr_3 formed in chlorinated groundwater with 1×10^{-4} mol/L bromide added (experimental phase D), as compared to groundwater with no bromide added (experimental phase A), at pH 7 and 9, at eight reaction times (hours), and at six chlorine concentrations.

The concentration of CHBr_3 increased at all six chlorine con-

TABLE 4.33

THE PERCENTAGE OF CHBr_3 FORMED IN CHLORINATED GROUND WATER WITH 1×10^{-6} mol/L BROMIDE ADDED (EXPERIMENTAL PHASE B) AS COMPARED TO GROUNDWATER WITH NO BROMIDE ADDED (EXPERIMENTAL PHASE A), AT pH 7 AND 9, AT EIGHT REACTION TIMES (HOURS), AND AT SIX CHLORINE CONCENTRATIONS

Chlorine Concentration Number	pH	Reaction Time (hours)							
		1	2	4	8	24	48	96	144
1	7	-42.4	-82.0	-25.2	-21.4	-7.14	+7.62	+11.4	+15.9
	9	+5.50	+0.95	+11.9	+18.6	+15.2	+17.8	+13.8	+18.8
2	7	-4.55	-0.43	+7.83	+12.1	+16.3	+28.8	+32.5	+35.6
	9	+36.8	+29.6	+19.6	+27.8	+47.4	+43.2	+41.4	+44.1
3	7	+135	+128	+127	+120	+129	+135	+148	+142
	9	+159	+165	+97.7	+103	+114	+118	+117	+135
4	7	+88.2	+99.6	+117	+117	+120	+140	+145	+147
	9	+106	+117	+124	+138	+145	+158	+168	+173
5	7	+198	+223	+230	+296	+342	+336	+353	+360
	9	+274	+294	+256	+328	+363	+367	+393	+381
6	7	+222	+240	+250	+279	+298	+290	+294	+325
	9	+244	+260	+277	+310	+351	+371	+361	+336

TABLE 4.34

THE PERCENTAGE OF CHBr_3 FORMED IN CHLORINATED GROUND WATER WITH 1×10^{-5} mol/L BROMIDE ADDED (EXPERIMENTAL PHASE C) AS COMPARED TO GROUNDWATER WITH NO BROMIDE ADDED (EXPERIMENTAL PHASE A), AT pH 7 AND 9, AT EIGHT REACTION TIMES (HOURS), AND AT SIX CHLORINE CONCENTRATIONS.

Chlorine Concentration Number	pH	Reaction Time (hours)							
		1	2	4	8	24	48	96	144
1	7	+19.0	+23.3	+25.5	+38.6	+47.6	+51.4	+49.1	+58.6
	9	+41.5	+41.9	+50.0	+45.5	+41.3	+51.3	+62.9	+66.3
2	7	+14.1	+12.6	+17.0	+17.9	+24.2	+27.1	+24.2	+28.0
	+	+86.8	+74.2	+58.9	+61.1	+65.9	+76.8	+71.0	+72.1
3	7	+128	+122	+118	+100	+112	+114	+110	+91.8
	9	+297	+167	+100	+104	+113	+122	+118	+113
4	7	+136	+127	+134	+127	+147	+145	+148	+156
	9	+142	+145	+147	+144	+146	+149	+149	+167
5	7	+1410	+1500	+1760	+1960	+2410	+2470	+2990	+3400
	9	+1920	+2110	+1870	+2160	+3090	+3140	+3510	+3550
6	7	+1700	+2020	+2030	+2420	+3420	+3590	+3860	+4450
	9	+2000	+2630	+3400	+3740	+4350	+4700	+5420	+5900

TABLE 4.35

THE PERCENTAGE OF CHBr_3 FORMED IN CHLORINATED GROUND WATER WITH 1×10^{-4} mol/L BROMIDE ADDED (EXPERIMENTAL PHASE D) AS COMPARED TO GROUNDWATER WITH NO BROMIDE ADDED (EXPERIMENTAL PHASE A), AT pH 7 AND 9, AT EIGHT REACTION TIMES (HOURS), AND AT SIX CHLORINE CONCENTRATIONS.

Chlorine Concentration Number	pH	Reaction Time (hours)							
		1	2	4	8	24	48	96	144
1	7	+352	+367	+373	+386	+433	+462	+459	+468
	9	+640	+629	+667	+695	+835	+874	+858	+913
2	7	+450	+439	+470	+488	+604	+621	+646	+632
	+	+632	+588	+533	+578	+759	+775	+800	+862
3	7	+1700	+1790	+1870	+1790	+2210	+2280	+2500	+2240
	9	+2650	+2860	+2210	+2390	+2680	+2780	+2760	+2700
4	7	+813	+865	+961	+1100	+1420	+1480	+1580	+1660
	9	+1320	+1430	+1590	+1650	+2020	+2240	+2300	+2400
5	7	+1900	+2010	+2210	+2410	+3030	+3470	+4010	+4130
	9	+5560	+6320	+6710	+8480	+10200	+11200	+13900	+14000
6	7	+4300	+5660	+6340	+9610	+11400	+11900	+15900	+18500
	9	+5440	+6420	+7360	+9040	+12200	+14100	+18600	+19400

centrations at all eight reaction times, the average percentage increase of CHBr_3 being much higher at chlorine concentrations 5 and 6.

TTHM: The effect of 1×10^{-6} mol/L bromide ion on the formation of TTHM in experimental phase B is shown in Table 4.36. The results are presented as the percentage of TTHM formed in chlorinated groundwater with 1×10^{-6} mol/L bromide added (experimental phase B), as compared to groundwater with no bromide added (experimental phase A), at pH 7 and 9, at eight reaction times (hours), and at six chlorine concentrations.

The concentration of TTHM increased at all six chlorine concentrations and at all eight reaction times with exception of chlorine concentrations 5, pH 7 at 4 hours reaction time.

The effect of 1×10^{-5} mol/L bromide ion on the TTHM concentration in experimental phase C is shown in Table 4.37. The results are presented as the percentage of TTHM formed in chlorinated groundwater with 1×10^{-5} mol/L bromide added (experimental phase C), as compared to groundwater with no bromide added (experimental phase A), at pH 7 and 9, at eight reaction times (hours), and at six chlorine concentrations.

The concentration of TTHM increased at all six chlorine concentrations and at all eight reaction times.

The effect of 1×10^{-4} mol/L bromide ion on the TTHM concentration in experimental phase D is shown in Table 4.38. The results are presented as the percentage of TTHM formed in chlorinated groundwater with 1×10^{-4} mol/L bromide added (experimental phase

TABLE 4.36

THE PERCENTAGE OF TTHM FORMED IN CHLORINATED GROUND WATER WITH 1×10^{-6} mol/L BROMIDE ADDED (EXPERIMENTAL PHASE B) AS COMPARED TO GROUNDWATER WITH NO BROMIDE ADDED (EXPERIMENTAL PHASE A), AT pH 7 AND 9, AT EIGHT REACTION TIMES (HOURS), AND AT SIX CHLORINE CONCENTRATIONS.

Chlorine Concentration Number	pH	Reaction Time (hours)							
		1	2	4	8	24	48	96	144
1	7	+55.6	+65.9	+63.0	+68.9	+87.4	+90.9	+95.1	+96.3
	9	+126	+131	+138	+145	+167	+177	+180	+183
2	7	+118	+114	+117	+119	+144	+130	+128	+126
	+	+180	+175	+138	+123	+153	+159	+163	+170
3	7	+155	+170	+171	+170	+217	+215	+231	+206
	9	+298	+293	+274	+294	+303	+308	+280	+264
4	7	+71.1	+71.3	+72.1	+72.7	+231	+219	+254	+243
	9	+55.9	+317	+323	+333	+378	+386	+376	+336
5	7	+22.4	+12.6	-4.60	+6.61	+21.3	+22.4	+44.8	+22.9
	9	+82.4	+72.4	+68.8	+74.8	+108	+136	+172	+180
6	7	+50.6	+46.6	+50.0	+66.5	+75.1	+85.1	+69.2	+70.8
	9	+73.4	+65.9	+64.8	+67.6	+75.1	+84.8	+112	+95.1

TABLE 4.37

THE PERCENTAGE OF TTHM FORMED IN CHLORINATED GROUND WATER WITH 1×10^{-5} mol/L BROMIDE ADDED (EXPERIMENTAL PHASE C) AS COMPARED TO GROUNDWATER WITH NO BROMIDE ADDED (EXPERIMENTAL PHASE A), AT pH 7 AND 9, AT EIGHT REACTION TIMES (HOURS), AND AT SIX CHLORINE CONCENTRATIONS.

Chlorine Concentration Number	pH	Reaction Time (hours)							
		1	2	4	8	24	48	96	144
1	7	+16.8	+19.5	+19.7	+24.2	+27.4	+33.9	+38.2	+37.9
	9	+25.3	+28.3	+30.6	+31.5	+35.8	+50.5	+51.7	+50.3
2	7	+37.4	+35.1	+38.0	+36.1	+35.3	+29.4	+27.9	+31.1
	+	+66.9	+88.4	+45.3	+35.0	+39.6	+42.1	+38.4	+38.3
3	7	+190	+186	+175	+167	+183	+269	+176	+161
	9	+249	+237	+214	+234	+211	+224	+206	+191
4	7	+396	+387	+379	+350	+356	+360	+355	+342
	9	+452	+419	+409	+406	+413	+408	+385	+367
5	7	+72.5	+59.7	+34.1	+30.0	+50.4	+58.2	+77.6	+86.4
	9	+58.5	+49.1	+32.1	+28.3	+67.7	+79.5	+94.9	+107
6	7	+46.3	+32.8	+30.3	+20.9	+41.2	+53.7	+28.1	+27.6
	9	+46.8	+46.5	+46.2	+35.3	+38.8	+48.1	+56.7	+46.6

TABLE 4.38

THE PERCENTAGE OF TTHM FORMED IN CHLORINATED GROUND WATER WITH 1×10^{-4} mol/L BROMIDE ADDED (EXPERIMENTAL PHASE D) AS COMPARED TO GROUNDWATER WITH NO BROMIDE ADDED (EXPERIMENTAL PHASE A), AT pH 7 AND 9, AT EIGHT REACTION TIMES (HOURS), AND AT SIX CHLORINE CONCENTRATIONS.

Chlorine Concentration Number	pH	Reaction Time (hours)							
		1	2	4	8	24	48	96	144
1	7	-35.3	-35.6	-28.4	-24.6	-15.4	-8.52	-4.47	-2.39
	9	+16.5	+17.1	+18.8	+22.6	+22.8	+37.1	+46.4	+46.5
2	7	+40.3	+39.0	+36.7	+38.6	+38.9	+36.0	+38.5	+39.2
	+	+62.8	+64.5	+41.0	+35.0	+37.7	+41.1	+39.3	+38.3
3	7	+93.0	+101	+92.6	+89.3	+89.7	+86.1	+87.4	+77.4
	9	+249	+233	+202	+210	+183	+178	+167	+167
4	7	+224	+209	+196	+180	+183	+172	+174	+190
	9	+338	+303	+287	+272	+260	+243	+222	+194
5	7	+10.9	+5.83	+6.55	+7.27	+34.7	+62.2	+71.6	+81.4
	9	+20.0	+17.9	+10.1	+11.0	+45.5	+90.9	+116	+136
6	7	-11.5	-17.8	-12.9	-16.5	+15.3	+25.5	+6.84	+5.84
	9	+16.5	+9.30	+10.3	+11.2	+21.5	+30.3	+28.5	+16.0

D), as compared to groundwater with no bromide added (experimental phase A), at pH 7 and 9, at eight reaction times (hours), and at six chlorine concentrations.

This study has shown that brominated THM's increase with increasing Br^- concentration. With an increase in Br^- concentration from 10^{-5} to 10^{-4} mol/L (at chlorine concentration 5 and 6) a major shift was observed in the distribution of THM's. The addition of a 1×10^{-6} mol/L bromide and 1×10^{-5} mol/L bromide (at chlorine concentration 1, 2, 3 and 4) had little effect on the distribution of THM's. However, it is interesting to note that the total concentration of THM's increased markedly with increasing bromide concentration in groundwater. Therefore, the presence of bromide ion in groundwater not only affects the distribution of the individual THM's but also influence their total concentration.

E. The Effect of pH on THM Formation: In chapter II the importance of pH on the formation of trihalomethanes during chlorination was discussed. The effect of pH upon trihalomethanes formation in chlorinated groundwater was studied at pH 7 and 9.

As stated previously the experimental design was divided into four phases, A, B, C and D. In experimental phase A no bromide was added to the groundwater. Bromide was added in experimental phase B, C and D, 1×10^{-6} mol/L, 1×10^{-5} mol/L and 1×10^{-4} mol/L bromide, respectively, prior to chlorination. In each experimental phase a sample of groundwater was adjusted to pH 7 or 9 prior to chlorination, as discussed in Chapter III. This section discusses the effect of pH of the formation of THM's.

Chloroform: The percentage of CHCl_3 formed in chlorinated groundwater buffered at pH 9, at eight reaction times (hours), as compared to pH 7, experimental phase A is presented in Table 4.39. The concentration of chloroform at chlorine concentration 1 (pH 9) showed little change as compared to pH 7. At chlorine concentration 2, the CHCl_3 concentration at pH 9 increased slightly at 1 hour and showed no change after 2 hours reaction time, an increase on the average of 28.2% was observed for 4 to 144 hours reaction time. The concentration of CHCl_3 , at chlorine concentration 3 showed no consistent trend with respect to pH 7. At chlorine concentration 4, the CHCl_3 concentration was not changed at pH 9 after 1 hour reaction time, but, increased on an average of 8.23% at the rest of the times. The effect of pH 9 on the CHCl_3 concentration at chlorine concentration 5 and 6 throughout all eight reaction times was an average increase of 11.9% and 13.4%, respectively.

The percentage of CHCl_3 formed in chlorinated groundwater buffered at pH 9, at eight reaction times (hours), as compared to pH 7, experimental phase B is presented in Table 4.40. The results in the table show that the concentration of CHCl_3 increased at pH 9 throughout eight reaction times at all chlorine concentrations. The average percentage increases were at chlorine concentration 1, 68.4%, chlorine concentration 2, 25.4%, chlorine concentration 3; 103%, chlorine concentration 4, 43.1%, chlorine concentration 5, 32.5%, and chlorine concentration 6, 35.5%.

The percentage of CHCl_3 formed in chlorinated groundwater buffered at pH 9, at eight reaction times (hours), as compared to pH

TABLE 4.39

THE PERCENTAGE OF CHCl_3 FORMED IN CHLORINATED GROUND WATER
 BUFFERED AT pH 9, AT EIGHT REACTION TIMES (HOURS), AS COMPARED
 TO pH 7, EXPERIMENTAL PHASE A.

Chlorine Concentration Number	Reaction Time (hours)							
	1	2	4	8	24	48	96	144
1	+4.76	+2.33	NC*	+2.27	+2.27	NC	NC	+4.44
2	+2.27	NC	+25.0	+33.3	+39.6	+23.0	+23.8	+24.6
3	-4.13	+2.44	+5.11	-2.68	+10.9	+5.78	+8.60	+3.77
4	NC	+9.26	+6.56	+2.90	+8.33	+6.33	+9.64	+14.6
5	+31.1	+25.9	+5.19	+10.0	+9.64	+8.24	+4.44	+1.05
6	+9.52	+13.5	+11.4	+9.09	+23.1	+32.1	+2.32	6.49

*No Change

TABLE 4.40

THE PERCENTAGE OF CHCl_3 FORMED IN CHLORINATED GROUND WATER
 BUFFERED AT pH 9, AT EIGHT REACTION TIMES (HOURS), AS COMPARED TO pH
 7, EXPERIMENTAL PHASE B.

Chlorine Concentration Number	Reaction Time (hours)							
	1	2	4	8	24	48	96	144
1	+78.1	+75.5	+60.5	+64.0	+60.7	+72.1	+67.3	+68.6
2	+14.3	+26.1	+30.2	+33.1	+31.5	+26.3	+23.6	+18.3
3	+135	+112	+106	+98.6	+96.0	+89.9	+90.4	+95.3
4	+51.6	+49.7	+48.5	+46.4	+40.8	+41.5	+34.9	+15.5
5	+42.0	+46.2	+41.2	+22.6	+17.1	+30.9	+31.4	+28.8
6	+62.1	+43.4	+37.2	+43.8	+25.0	+29.8	+26.1	+16.7

7, experimental phase C are presented in Table 4.41. The concentration of CHCl_3 had no change at chlorine concentration 4 after 4 hours reaction time, but, increased after 1, 2, 8, 24, 48, 96 and 144 hours reaction time an average of 5.70%. The concentration of CHCl_3 increased throughout all eight reaction times at pH 9 for chlorine concentrations 1, 2, 3, 4, 5 and 6. The average percentage increase observed was at chlorine concentration 1, 11.9%, chlorine concentration 2, 29.4%, chlorine concentration 3, chlorine concentration 4, chlorine concentration 5, 18.6% and chlorine concentration 6, 13.4%.

In Table 4.42 the percentage of CHCl_3 formed in chlorinated groundwater buffered at pH 9 at eight reaction times (hours), as compared to pH 7, experimental phase D is presented. The results in Table 4.42 reveal that the concentration of CHCl_3 at pH 9 was greater than that at pH 7 at all eight reaction times and all chlorine concentrations. The average percentage increase was at chlorine concentration 1, 23.4%, chlorine concentration 2, 38.2%, chlorine concentration 3, 12.3%, chlorine concentration 4, 22.7%, chlorine concentration 5, 20.8% and chlorine concentration 6, 40.1%.

Bromodichloromethane: The percentage of CHCl_2Br formed in chlorinated groundwater buffered at pH 9, at eight reaction times (hours), as compared to pH 7 experimental phase A is presented in Table 4.43. The concentration of CHCl_2Br at chlorine concentration 1 showed little change at all reaction times. However, chlorine concentration 2, the CHCl_2Br concentration increased at all but the last reaction time an average of 9.86%. At chlorine concentration 3

TABLE 4.41

THE PERCENTAGE OF CHCl_3 FORMED IN CHLORINATED GROUND WATER
 BUFFERED AT pH 9, AT EIGHT REACTION TIMES (HOURS), AS COMPARED
 TO pH 7, EXPERIMENTAL PHASE C.

Chlorine Concentration Number	Reaction Time (hours)							
	1	2	4	8	24	48	96	144
1	+11.7	+7.63	+5.72	+4.47	+11.7	+18.7	+16.1	+19.0
2	+33.1	+20.0	+33.4	+33.5	+40.1	+31.3	+27.8	+16.1
3	+14.4	+15.3	+12.6	+13.6	+9.62	+11.7	+9.98	+4.91
4	+12.3	+4.81	NC*	+1.76	+4.46	+3.64	+2.26	+10.7
5	+11.0	+17.5	+22.7	+27.2	+25.2	+17.6	+9.59	+17.9
6	+13.6	+9.02	+10.8	+14.3	+5.61	+12.8	+20.4	+20.3

*NO CHANGE

TABLE 4.42.

THE PERCENTAGE OF CHCl_3 FORMED IN CHLORINATED GROUND WATER
 BUFFERED AT pH 9 AT EIGHT REACTION TIMES (HOURS), AS COMPARED
 TO pH 7 EXPERIMENTAL PHASE D

Chlorine Concentration Number	Reaction Time (hours)							
	1	2	4	8	24	48	96	144
1	+75.9	+30.8	+24.1	+20.8	+3.56	+5.40	+8.72	+18.3
2	+46.2	+46.1	+44.3	+43.3	+35.7	+31.3	+30.2	+28.4
3	+21.3	+20.4	+16.4	+14.6	+11.0	+7.25	+3.17	+4.00
4	+24.2	+21.7	+25.3	+29.5	+19.6	+20.0	+20.0	+20.9
5	+23.5	+22.7	+20.4	+20.5	+17.1	+18.2	+22.4	+21.9
6	+15.8	+17.9	+20.2	+22.2	+20.9	+13.2	+14.3	+13.6

TABLE 4.43

THE PERCENTAGE OF CHCl_2Br FORMED IN CHLORINATED GROUND WATER
 BUFFERED AT pH 9, AT EIGHT REACTION TIMES (HOURS), AS COMPARED
 TO pH 7, EXPERIMENTAL PHASE A.

Chlorine Concentration Number	Reaction Time (hours)							
	1	2	4	8	24	48	96	144
1	+4.76	+4.76	NC*	-4.35	+12.0	+12.0	+7.69	+3.70
2	+8.33	+16.0	+24.0	+19.2	+14.3	+10.3	+6.45	NC
3	+10.0	+15.2	+8.57	+2.63	-2.44	+4.65	+11.1	+13.0
4	-3.85	-10.7	-13.8	-16.1	-18.2	-5.88	-5.26	+7.14
5	+16.7	+14.3	+11.8	+34.1	+7.69	-3.39	-1.59	-3.08
6	+36.1	+3.98	+1.41	-1.64	+2.44	+2.41	-1.12	-2.83

*NO CHANGE

at pH 9 the concentration of CHCl_2Br increased an average of 9.31%, except after 24 hours reaction where it decreased by 2.44%. At chlorine concentration 4 the concentration of CHCl_2Br decreased an average of 10.5%, but, increased by 7.14% after 144 hours reaction time. The CHCl_2Br concentration at pH 9, chlorine concentration 5, increased at all reaction times through 24, hours an average of 16.9%, and then decreased after 48, 96 and 144 hours reaction time an average of 2.69%. At chlorine concentration 6 the concentration of CHCl_2Br at pH 9 showed no change relative to pH 7.

The percentage of CHCl_2Br formed in chlorinated groundwater buffered at pH 9, at eight reaction times (hours), as compared to pH 7, experimental phase A is presented in Table 4.44. The concentration of CHCl_2Br increased at pH 9 throughout eight reaction times at all chlorine concentrations. The average percentage increase of CHCl_2Br was at chlorine concentration 1, 87.7%, chlorine concentration 2, 9.11%, chlorine concentration 3, 24.7%, chlorine concentration 4, 15.4%, chlorine concentration 5, 24.5% and chlorine concentration 6, 39.4%.

In Table 4.45 the percentage of CHCl_2Br formed in chlorinated groundwater buffered at pH 9, at eight reaction times (hours) as compared to pH 7 are presented. The concentration of CHCl_2Br increased at pH 9 throughout the eight reaction times at all chlorine concentrations. The average percentage increase was at chlorine concentration 1, 8.21%, chlorine concentration 2, 15.1%, chlorine concentration 3, 33.2%, chlorine concentration 4, 31.4%, chlorine concentration 5, 9.89% and chlorine concentration 6, 12.7%.

TABLE 4.44

THE PERCENTAGE OF CHCl_2Br FORMED IN CHLORINATED GROUND WATER
 BUFFERED AT pH 9, AT EIGHT REACTION TIMES (HOURS), AS COMPARED
 TO pH 7, EXPERIMENTAL PHASE B.

Chlorine Concentration Number	Reaction Time (hours)							
	1	2	4	8	24	48	96	144
1	+97.4	+102	+100	+86.5	+82.0	+75.9	+84.6	+72.9
2	+11.7	+14.2	+13.8	+7.43	+7.39	+6.68	+6.69	+4.95
3	+27.7	+28.3	+28.5	+23.7	+22.3	+19.7	+23.6	+24.1
4	+22.8	+19.5	+17.0	+14.7	+17.4	+17.1	+8.88	+5.62
5	+20.5	+28.9	+24.1	+17.6	+13.7	+11.6	+33.7	+45.5
6	+62.1	+69.2	+46.5	+51.5	+30.2	+24.6	+19.8	+11.5

TABLE 4.45

THE PERCENTAGE OF CHCl_2Br FORMED IN CHLORINATED GROUND WATER
 BUFFERED AT pH 9, AT EIGHT REACTION TIMES (HOURS), AS COMPARED
 TO pH 7, EXPERIMENTAL PHASE C.

Chlorine Concentration Number	Reaction Time (hours)							
	1	2	4	8	24	48	96	144
1	+10.1	+11.6	+6.84	+4.61	+14.3	+10.1	+3.84	+4.27
2	+6.60	+11.3	+14.5	+15.6	+16.5	+16.5	+17.9	+22.1
3	+24.3	+30.1	+37.8	+41.5	+31.7	+33.7	+33.3	+32.9
4	+14.5	+22.5	+25.8	+32.1	+43.4	+40.2	+37.6	+34.7
5	+5.19	+6.99	+2.91	+12.9	+13.2	+8.90	+11.1	+17.9
6	+19.4	+13.3	+7.55	+1.52	+12.6	+20.0	+16.2	+11.0

The percentage of CHCl_2Br formed in chlorinated groundwater buffered at pH 9 and at eight reaction time (hours), as compared to pH 7, experimental phase D are shown in Table 4.46. The concentration of CHCl_2Br increased at pH 9 throughout all eight reaction times and at all chlorine concentrations. The average percentage increase was at chlorine concentration 1, 16.7%, chlorine concentration 2, 18.6%, chlorine concentration 3, 48.3%, chlorine concentration 4, 52.6%, chlorine concentration 5, 22.7% and chlorine concentration 6, 42.8%.

Chlorodibromomethane: Table 4.47 presents the percentage of CHClBr_2 formed in chlorinated groundwater buffered at pH 9, at eight reaction times (hours), as compared to pH 7, experimental phase A. The concentration of CHClBr_2 showed no consistent trend at pH 9 as compared to pH 7 for chlorine concentration 1 to 5. At chlorine concentration 6, pH 9, the CHClBr_2 concentration increased throughout eight reaction times an average of 24.3%.

Table 4.48 presents the percentage of CHClBr_2 formed in chlorinated groundwater buffered at pH 9, at eight reaction times (hours), as compared to pH 7, experimental phase B. The concentration of CHClBr_2 increased at pH 9 throughout eight reaction times at chlorine concentration 1, 2, 4, 5 and 6. The average percentage increase was at chlorine concentration 1, 26.9%, chlorine concentration 2, 33.2%, chlorine concentration 4, 10.1%, chlorine concentration 5, 25.1% and chlorine concentration 6, 29.6%. The concentration of CHClBr_2 at chlorine concentration 3, pH 9, increased most significantly after 1 hour then tended to increase less with time and finally decreased after 96 and 144 hours reaction time

TABLE 4.46

THE PERCENTAGE OF CHCl_2Br FORMED IN CHLORINATED GROUND WATER
 BUFFERED AT pH 9, AT EIGHT REACTION TIMES (HOURS), AS COMPARED
 TO pH 7, EXPERIMENTAL PHASE D.

Chlorine Concentration Number	Reaction Time (hours)							
	1	2	4	8	24	48	96	144
1	+16.8	+17.7	+21.7	+19.1	+16.0	+16.0	+13.2	+12.7
2	+24.8	+20.8	+21.1	+20.1	+15.7	+16.8	+14.8	+14.3
3	+51.8	+54.2	+53.9	+49.1	+46.7	+46.7	+41.9	+42.4
4	+50.0	+52.8	+56.8	+55.0	+45.6	+49.1	+53.8	+57.3
5	+43.7	+29.3	+15.6	+10.1	+9.34	+16.8	+26.8	+30.1
6	+48.4	+44.7	+44.1	+42.4	+35.1	+31.7	+48.4	+47.4

TABLE 4.47

THE PERCENTAGE OF CHClBr_2 FORMED IN CHLORINATED GROUND WATER
 BUFFERED AT pH 9, AT EIGHT REACTION TIMES (HOURS), AS COMPARED
 TO pH 7 EXPERIMENTAL PHASE A.

Chlorine Concentration Number	Reaction Time (hours)							
	1	2	4	8	24	48	96	144
1	NC*	NC	+4.76	+8.70	+4.35	+8.33	NC	NC
2	+15.0	+9.09	+12.9	+8.40	+7.69	+3.70	+14.3	+13.8
3	+6.45	NC	-2.94	-8.11	-7.89	-10.3	-7.50	-9.52
4	+4.55	NC	-4.00	-11.1	-7.41	-7.14	-3.45	-9.68
5	+11.9	+48.8	+46.7	+8.50	-0.54	NC	+6.77	+18.3
6	+10.6	+23.5	+33.3	+27.7	+35.5	+20.7	+18.7	+24.7

*NO CHANGE

TABLE 4.48

THE PERCENTAGE OF CHClBr_2 FORMED IN CHLORINATED GROUND WATER
 BUFFERED AT pH 9, AT EIGHT REACTION TIMES (HOURS), AS COMPARED
 TO pH 7, EXPERIMENTAL PHASE B.

Chlorine Concentration Number	Reaction Time (hours)							
	1	2	4	8	24	48	96	144
1	+52.1	+50.9	+37.3	+28.4	+13.9	+10.0	+11.0	+11.2
2	+51.2	+36.1	+32.7	+31.3	+33.4	+29.2	+28.0	+23.9
3	+17.4	+15.2	+8.13	+5.06	+9.16	+0.14	-8.15	-5.09
4	+11.3	+13.9	+9.72	+8.32	+8.69	+8.48	+9.87	+10.9
5	+49.7	+44.1	+15.4	+11.2	+18.6	+5.88	+18.8	+37.3
6	+40.6	+44.4	+54.9	+37.3	+16.9	+18.4	+11.7	+12.4

relative to pH 7.

Table 4.49 presents the percentage of CHClBr_2 formed in chlorinated groundwater buffered at pH 9, at eight reaction times (hours) as compared to pH 7, experimental phase C. Table 4.49 reveals that the concentration of CHClBr_2 increased, at pH 9, at chlorine concentrations 1, 2, 3, 5 and 6 throughout all eight reaction times. The average percentage increase was at chlorine concentration 1, 9.89%, chlorine concentration 2, 19.1%, chlorine concentration 3, 47.1%, chlorine concentration 5, 16.1% and chlorine concentration 6, 13.3%. At chlorine concentration 4, there appeared no change relative to pH 7.

Table 4.50 presents the percentage of CHClBr_2 formed in chlorinated groundwater buffered at pH 9, at eight reaction times (hours), as compared to pH 7, experimental phase D. Inspection of Table 4.50 reveals that the concentration of CHClBr_2 increased throughout all eight reaction times at all chlorine concentrations. The average percentage increase was at chlorine concentration 1, 53.3%, chlorine concentration 2, 41.2%, chlorine concentration 3, 38.6%, chlorine concentration 4, 49.5%, chlorine concentration 5, 43.2% and chlorine concentration 6, 35.5%.

Bromoform: Table 4.51 presents the percentage of CHBr_3 formed in chlorinated groundwater buffered at pH 9, at eight reaction times (hours), as compared to pH 7, experimental phase A. The concentration of CHBr_3 at pH 9 showed no consistent pattern relative to pH 7, sometimes increasing and sometimes decreasing.

Table 4.52 presents the percentage of CHBr_3 formed in

TABLE 4.49

THE PERCENTAGE OF CHClBr_2 FORMED IN CHLORINATED GROUND WATER
 BUFFERED AT pH 9, AT EIGHT REACTION TIMES (HOURS), AS COMPARED
 TO pH 7, EXPERIMENTAL PHASE C.

Chlorine Concentration Number	Reaction Time (hours)							
	1	2	4	8	24	48	96	144
1	+7.12	+7.64	+8.13	+3.50	+7.84	+12.7	+16.0	+16.2
2	+18.9	+17.3	+14.2	+10.9	+19.0	+20.8	+21.6	+29.7
3	+45.1	+44.3	+41.0	+49.9	+47.7	+49.1	+50.9	+48.9
4	+3.94	+2.69	+2.13	+1.29	-0.16	+0.15	-1.45	+0.14
5	+24.5	+17.6	+5.58	+7.32	+20.8	+21.1	+16.9	+15.2
6	+15.0	+15.1	+12.7	+9.22	+16.2	+9.42	+19.3	+9.09

TABLE 4.50

THE PERCENTAGE OF CHClBr_2 FORMED IN CHLORINATED GROUND WATER
BUFFERED AT pH 9, AT EIGHT REACTION TIMES (HOURS), AS COMPARED
TO pH 7, EXPERIMENTAL PHASE D.

Chlorine Concentration Number	Reaction Time (hours)							
	1	2	4	8	24	48	96	144
1	+54.5	+52.8	+55.0	+53.8	+54.7	+55.2	+53.8	+46.3
2	+31.3	+38.3	+39.7	+33.7	+32.4	+32.7	+66.1	+55.0
3	+61.4	+57.4	+47.1	+40.4	+33.6	+27.4	+20.0	+21.6
4	+39.9	+42.2	+47.6	+64.9	+58.6	+56.1	+45.9	+40.7
5	+38.4	+38.0	+33.7	+37.0	+44.7	+47.9	+46.8	+59.2
6	+33.6	+30.7	+29.1	+38.6	+42.1	+37.6	+43.5	+29.1

TABLE 4.51

THE PERCENTAGE OF CHBr_3 FORMED IN CHLORINATED GROUND WATER
 BUFFERED AT pH 9, AT EIGHT REACTION TIMES (HOURS), AS COMPARED
 TO pH 7, EXPERIMENTAL PHASE A.

Chlorine Concentration Number	Reaction Time (hours)							
	1	2	4	8	24	48	96	144
1	-4.76	NC*	NC	+4.76	+9.52	+9.52	+9.09	+9.09
2	NC	+4.35	+17.4	+12.5	+12.5	+16.7	+20.8	+16.0
3	+4.55	NC	+29.1	+14.8	+18.5	+14.3	+13.8	+3.03
4	+9.09	+4.35	+4.35	+4.17	+4.17	NC	+4.00	+4.00
5	-12.5	-10.0	NC	-4.44	-4.44	-2.13	-2.13	NC
6	+6.67	+6.67	NC	+2.08	+2.08	NC	+5.88	+9.43

*NO CHANGE

TABLE 4.52

THE PERCENTAGE OF CHBr_3 FORMED IN CHLORINATED GROUND WATER
 BUFFERED AT pH 9, AT EIGHT REACTION TIMES (HOURS), AS COMPARED
 TO pH 7, EXPERIMENTAL PHASE B.

Chlorine Concentration Number	Reaction Time (hours)							
	1	2	4	8	24	48	96	144
1	+74.4	+73.8	+49.7	+58.2	+35.9	+19.9	+11.4	+11.8
2	+43.3	+35.8	+30.3	+28.3	+42.7	+29.8	+28.9	+23.3
3	+14.9	+16.2	+12.7	+5.71	+10.8	+6.07	-0.42	-0.13
4	+19.6	+13.5	+8.03	+14.0	+15.7	+7.51	+14.0	+14.9
5	+10.1	+10.1	+7.75	+3.37	NC*	+4.88	+6.57	+4.52
6	+13.8	+13.1	+7.74	+10.4	+15.7	+20.6	+23.9	+12.4

*NO CHANGE

chlorinated groundwater buffered at pH 9, at eight reaction times (hours), as compared to pH 7 (experimental phase B). The concentration of CHBr_3 at chlorine concentration 1 and 2, pH 9, increased throughout the eight reaction times an average of 41.9% and 32.8%, respectively. At chlorine concentration 3, pH 9, the CHBr_3 concentration increased at 1, 2, 4, 8, 24 and 48 hours reaction time an average of 8.30%, but, decreased slightly after 96 and 144 hours reaction time. The concentration of CHBr_3 at pH 9, at chlorine concentration 4 increased throughout eight reaction times an average of 13.4%. At chlorine concentration 5, pH 9, CHBr_3 concentration had no change after 24 hours reaction time, but increased an average of 6.76% after 1, 1, 4, 8, 48, 96 and 144 hours reaction times. The concentration of CHBr_3 at chlorine concentration 6, pH 9, increased throughout the eight reaction times an average of 14.7%.

Table 4.53 presents the percentage of CHBr_3 formed in chlorinated groundwater buffered at pH 9, eight reaction times (hours), as compared to pH 7, experimental phase C. Table 4.53 reveals that the concentration of CHBr_3 increased throughout eight reaction times at all chlorine concentrations. The average percentage increase of CHBr_3 was 13.2%; at chlorine concentration 1, 59.2%; at chlorine concentration 2, 18.5%; at chlorine concentration 3, 8.21%; at chlorine concentration 4, 14.4%; at chlorine concentration 5, and 41.7%; at chlorine concentration 6. Table 4.54 presents the percentage of CHBr_3 formed in chlorinated groundwater buffered at pH 9, at eight reaction times (hours), as compared to pH 7, experimental phase D. Table 4.54 reveals that the concentration of

TABLE 4.53

THE PERCENTAGE OF CHBr_3 FORMED IN CHLORINATED GROUND WATER
 BUFFERED AT pH 9, AT EIGHT REACTION TIMES (HOURS), AS COMPARED
 TO pH 7, EXPERIMENTAL PHASE C.

Chlorine Concentration Number	Reaction Time (hours)							
	1	2	4	8	24	48	96	144
1	+13.2	+15.1	+19.8	+9.97	+4.84	+9.43	+19.2	+14.3
2	+63.7	+61.4	+59.5	+53.7	+50.3	+62.3	+66.4	+55.9
3	+22.0	+20.4	+19.0	+16.6	+18.8	+18.7	+17.7	+14.5
4	+11.8	+12.8	+10.2	+12.1	+3.89	+1.63	+4.48	+8.76
5	+17.4	+24.0	+5.76	+5.19	+21.2	+23.1	+14.5	+4.17
6	+25.0	+37.5	+64.7	+55.4	+29.0	+30.3	+47.5	+44.4

TABLE 4.54

THE PERCENTAGE OF CHBr_3 FORMED IN CHLORINATED GROUND WATER
 BUFFERED AT pH 9, AT EIGHT REACTION TIMES (HOURS), AS COMPARED
 TO pH 7, EXPERIMENTAL PHASE D.

Chlorine Concentration Number	Reaction Time (hours)							
	1	2	4	8	24	48	96	144
1	+54.5	+52.8	+55.0	+53.8	+54.7	+55.2	+53.8	+46.3
2	+33.1	+33.1	+30.5	+29.8	+37.3	+41.6	+45.8	+52.5
3	+60.3	+56.6	+51.5	+50.9	+42.5	+38.3	+25.5	+23.6
4	+69.7	+65.3	+66.0	+51.6	+44.9	+47.9	+48.7	+47.7
5	+147	+173	+194	+227	+215	+211	+234	+234
6	+34.3	+20.8	+15.9	+3.86	+9.21	+18.3	+23.6	+14.7

CHBr_3 at pH 9 increased throughout all eight reaction times at all chlorine concentrations. The average percentage increase was 53.3% at chlorine concentration 1, 38.0% at chlorine concentration 2, 43.7% at chlorine concentration 3, 55.2% at chlorine concentration 4, 204% at chlorine concentration 5 and 17.6% at chlorine concentration

TTHM: Table 4.55 presents the percentage of TTHM formed in chlorinated groundwater buffered at pH 9, at eight reaction times (hours) as compared to pH 7, experimental phase A. At chlorine concentration 1, 3 and 4, pH 9, the concentration of TTHM show no consistent pattern relative to pH 7. The TTHM concentration at chlorine concentration 2, pH 9, increased throughout eight reaction times an average of 17.4%. The concentration of TTHM increased throughout eight reaction times at chlorine concentration 5 and 6, pH 9, an average of 11.6% and 11.9%, respectively. The relative increase, decreasing with reaction time.

Table 4.56 presents the percentage of TTHM formed in chlorinated groundwater buffered at pH 9, at eight reaction times (hours), as compared to pH 7, experimental phase B. Table 4.56 reveals that the concentration of TTHM increased throughout eight reaction times at all chlorine concentrations. The average percentage increase was 62.3% at chlorine concentration 1, 22.4% at chlorine concentration 2, 62.9% at chlorine concentration 3, 28.1% at chlorine concentration 4, 28.2% at chlorine concentration 5 and 34.6% at chlorine concentration.

Table 4.57 presents the percentage of TTHM formed in chlorinated groundwater buffered at pH 9, at eight reaction times (hours), as

TABLE 4.55

THE PERCENTAGE OF TTHM FORMED IN CHLORINATED GROUND WATER
 BUFFERED AT pH 9, AT EIGHT REACTION TIMES (HOURS), AS COMPARED
 TO pH 7, EXPERIMENTAL PHASE A.

Chlorine Concentration Number	Reaction Time (hours)							
	1	2	4	8	24	48	96	144
1	+2.93	+2.28	-0.73	-0.57	+4.06	+2.20	+2.71	+4.11
2	+3.87	+5.18	+22.1	+28.6	+26.9	+17.3	+18.4	+16.9
3	-0.70	+3.38	+6.17	-1.69	+7.57	+3.48	+7.48	+3.77
4	-0.91	-3.17	-0.99	+2.38	-0.96	-1.79	-4.10	-9.49
5	+24.5	+24.9	+11.6	+15.5	+7.44	+3.94	+2.99	+2.14
6	+18.1	+11.2	+9.85	+7.59	+18.1	+22.9	+2.66	+5.19

TABLE 4.56

THE PERCENTAGE OF TTHM FORMED IN CHLORINATED GROUND WATER
 BUFFERED AT pH 9, AT EIGHT REACTION TIMES (HOURS), AS COMPARED
 TO pH 7, EXPERIMENTAL PHASE B.

Chlorine Concentration Number	Reaction Time (hours)							
	1	2	4	8	24	48	96	144
1	+78.0	+78.5	+64.6	+62.4	+53.6	+54.5	+54.4	+52.7
2	+20.5	+24.5	+26.0	+25.2	+25.9	+21.8	+19.1	+16.1
3	+79.7	+71.4	+66.7	+60.9	+60.4	+54.5	+53.4	+55.9
4	+36.4	+34.5	+32.0	+30.0	+28.5	+28.4	+22.4	+12.3
5	+34.7	+39.1	+31.4	+19.5	+16.0	+22.3	+29.6	+32.7
6	+55.4	+48.0	+39.1	+43.2	+24.5	+27.5	+23.5	+15.3

TABLE 4.57

THE PERCENTAGE OF THM FORMED IN CHLORINATED GROUND WATER
 BUFFERED AT pH 9, AT EIGHT REACTION TIMES (HOURS), AS COMPARED
 TO pH 7, EXPERIMENTAL PHASE C.

Chlorine Concentration Number	Reaction Time (hours)							
	1	2	4	8	24	48	96	144
1	+10.4	+9.81	+8.26	+5.28	+10.9	+14.9	+12.7	+13.5
2	+26.2	+31.0	+28.6	+27.5	+31.0	+28.8	+28.1	+23.3
3	+19.5	+21.5	+21.1	+23.0	+18.2	+20.1	+19.1	+15.5
4	+12.4	+9.95	+7.19	+9.87	+13.6	+12.5	+11.3	+16.6
5	+14.4	+16.5	+9.92	+14.0	+19.8	+17.9	+13.0	+13.4
6	+18.5	+22.7	+23.3	+20.4	+16.0	+18.3	+25.5	+20.9

compared to pH 7, experimental phase C. Table 4.57 reveals that the concentration of TTHM increased throughout eight reaction times at all chlorine concentrations. The average percentage increase was 10.7% at chlorine concentration 1, 28.1% at chlorine concentration 2, 19.8% at chlorine concentration 3, 11.7% at chlorine concentration 4 14.9% at chlorine concentration 5 and 20.7% at chlorine concentration 6

Table 4.58 presents the percentage of TTHM formed in chlorinated groundwater buffered at pH 9, at eight reaction times (hours), as compared to pH 7, experimental phase D. Table 4.58 reveals that the concentration of TTHM increased throughout eight reaction times at all chlorine concentrations. The average percentage increase was 47.2% at chlorine concentration 1, 34.0% at chlorine concentration 2, 39.2% at chlorine concentration 3, 48.2% at chlorine concentration 4, 109% at chlorine concentration 5 and 22.9% at chlorine concentration 6.

TABLE 4.58

THE PERCENTAGE OF TTHM FORMED IN CHLORINATED GROUND WATER
 BUFFERED AT pH 9, AT EIGHT REACTION TIMES (HOURS), AS COMPARED
 TO pH 7, EXPERIMENTAL PHASE D.

Chlorine Concentration Number	Reaction Time (hours)							
	1	2	4	8	24	48	96	144
1	+49.5	+42.2	+44.6	+47.4	+48.5	+48.2	+47.2	+50.0
2	+33.6	+35.0	+33.9	+31.4	+31.4	+31.9	+36.1	+39.0
3	+54.8	+52.5	+46.5	+43.3	+36.6	+33.8	+23.1	+23.2
4	+49.3	+49.2	+53.0	+53.5	+45.7	+47.8	+45.3	+41.5
5	+85.6	+91.1	+97.4	+111	+109	+114	+129	+133
6	+36.0	+25.9	+23.2	+8.36	+18.1	+22.7	+28.8	+20.2

V. CONCLUSION

In ground water to which no bromide had been added (experimental phase A) chloroform was the predominant trihalomethane formed. Brominated THM's were observed indicating that some bromide was present in the natural ground water. On a mole basis CHCl_3 was 50-75% of the total THM's, while CHCl_2Br , CHClBr_2 and CHBr_3 , were 15-30%, 10-15% and 0.50-10%, respectively.

In experimental phase B 1×10^{-6} mol/L bromide was added to ground water. In spite of 1×10^{-6} mol/L bromide, chloroform was dominant component, usually comprising 40-60% of the THM content on a mole basis. Correspondingly, bromodichloromethane and chlorodibromomethane contents were, 20-28% and 10-20%, respectively. Bromoform contents were 4-15%

In experimental phase C the presence of 1×10^{-5} mol/L bromide caused an increase in the yield of brominated THM's. On a mole basis, chloroform (CHCl_3) was the dominant component, at chlorine concentrations 1, 2, 3 and 4, comprising 40-60% but only 20-30% of the THM content at chlorine concentration 5 and 6. Bromodichloromethane and chlorodibromomethane contents were, 25-32% and 10-30%, respectively, at all chlorine concentrations. Bromoform concentration 1, 2, 3, and 4 and 20-30% at chlorine concentration 5 and 6.

In ground water to which 1×10^{-4} mol/L bromide had been added (experimental phase D) a significant increased on a mole and ug/L basis of brominated THM's was observed. Associated with this was

a substantial reduction in the CHCl_3 concentration. Bromoform was the dominant component in experimental phase D, comprising 30-75%. Correspondingly, chlorodibromomethane and bromodichloromethane contents were, 15-35% and 10-25%, of the total respectively, while chloroform comprised only 1-25%.

Throughout the experimental phases increasing the pH at which the reaction was carried out, 7 and 9, an increase of THM's were observed. In every experiment an increase in time resulted in an increase in THM concentration. The rate of increase varied as a function of chlorine concentration and pH.

In general an increase in chlorine resulted in an increase in the yield of THM's. The exception to this was the chlorine concentration corresponding to the breakpoint, where the yield of THM's was suppressed relative to chlorine concentrations immediately before and after the breakpoint. This phenomenon is not yet understood.

LITERATURE CITED

- Amy, G. 1983. Personal Communication, University of Arizona, Tucson, AZ.
- Anon. 1978. Control of Organic Chemical Contaminants in Drinking Water, Federal Register 43 (No. 28): 5756-5780.
- Anon. 1979. National Interim Primary Drinking Water Regulations, Control of Trihalomethanes in Drinking Water; Final Rule. Federal Register 44 (No. 231): 68624-68701.
- Arguello, M. D.; C. D. Chriswell; J. S. Fritz; L. D. Kissinger; K. W. Lee; J. J. Richard; H. J. Svec. 1979. Trihalomethanes in Water: A Report on the Occurrence, Seasonal Variation in Concentration and Precursors of Trihalomethanes. J. Am. Water Works Assoc. 71: 504.
- Babcock, D. B.; P. C. Singer. 1979. Chlorination and Coagulation of Humic and Fulvic Acids. J. Am. Water Works Assoc. 71: 149-152.
- Beeman, C.; R. Lang; D. F. Jackson. 1978. Survey of Trihalomethane Distribution in Various Potable Water Supply Sources in the State of Florida. For Bureau of Drinking Water and Special Programs, Florida Dept. of Env. Reg., Tallahassee, FL.
- Bird, J. C. 1979. The Effect of Bromide on Trihalomethane Formation. M.S. Thesis, The University of Tennessee, Knoxville, TN.
- Brass, H. J.; M. A. Fiege; T. Halloran; J. W. Mell; D. Munch; R. F. Thomas. 1977. The National Organic Monitoring Survey: Sampling and Analyses for Purgeable Organic Compounds. In: Drinking Water Quality Enhancement Through Source Protection. ed. R. B. Pojasek, Ann Arbor Science Publishers, Inc., Ann Arbor, MI., 393-416 pp.
- Brett, R. W.; R. A. Calverly. 1979. A one year survey of Trihalomethane Concentration Changes within a Distribution system. J. Am. Water Works Assoc. 71: 515-520.
- Bull, R. J. 1980. Health Effects of Alternative Disinfectants and Their Reaction Products. J. Am. Water Works Assoc. 72: 299.
- Bunn, W. W.; B. B. Haas; E. R. Deane; R. D. Kleopfer. 1975. Formation of Trihalomethanes by Chlorination of Surface Water. Environmental Letters. 10-205 pp.
- Carus, K. E.; K. B. Stinson. 1978. Controlling Organics: The East Bay Municipal Utility District Experience. J. Am. Water Works Assoc. 70: 637.
- Christman, R. E.; M. Ghassami. 1966. Chemical Nature of Organic Color in Water. J. Am. Water Works Assoc. 58: 723-741.

Cooper, W. J.; C. A. Sorber and E. P. Meier. 1975. "A Rapid Specific Free Available Chlorine Test with Syringaldazine (FACTS), J. Am. Waters Assoc. 67, 34.

Cooper, W. J.; L. M. Meyer; C. C. Bofill; E. Cordall. 1981. The Quantitative Effects of Bromine on the Formation and Distribution of Trihalomethanes in a Ground Water with a High Organic Content. To be presented at the 4th Water Chlorination Conference. (Oct. 18-23, 1981).

Cotruvo, J.; H. Sontheimer. 1979. Practical Applications of Absorption Techniques in Drinking Water. Conference held at Reston, VA. April 30 - May 2, 1979 (In Press).

Engerholm, A. B. 1981. A Predictive Model for Chloroform Formation from Humic Substances. Ph.D. Thesis. The University of Arizona. 15-20 pp.

Haag, W. 1980. The Formation of N-Bromo-N-Chloramines in Chlorinated Saline Waters. J. Inorg. Nucl. Chem., 42: 1123.

Johnson, D. J.; G. W. Imman. 1978. The Kinetics of Chlorine-Ammonia Reactions in Sea Water. University of North Carolina 1-66 pp.

Kavanaugh, M. C.; R. R. Trussell. 1980. Design of Aeration Towers to Strip Volatile Contaminants from Drinking Water. J. Am. Water Works Assoc. 72: 684-692.

Kuhn, W.; H. Sontheimer. 1979. Oxidation Techniques in Drinking Water Pilot Project. Report IIA, Advanced Treatment Technology. US EPA, Office of Drinking Water, Wash., D. C. EPA 570/9-79-020 CCMS II.

Lange, A. L.; E. Kawczynski. 1978. Controlling Organics: The Contra Costa County Water District Experience. J. Am. Water Works Assoc. 70: 653-659.

Love, O. T.; J. K. Carswell; R. J. Miltner; J. M. Symons. 1976. Treatment for the Prevention or Removal of Trihalomethanes in Drinking Water. Appendix 3 to Interim Treatment Guide for the Control of Chloroform and Other Trihalomethanes, unpublished.

Minear, R. A. 1981. Bromide, the Missing Factor in THM Formation and Removal, Prediction. Water Industry '81. Presented at International Conference Brighton, UK, June 1981. 106-113 pp.

Morris, J. C.; N. Raum; B. Raum; E. Wajon. 1980. Formation and Significance of N. Chloro Compounds in Water Supplies. EPA-600/2-80-031, MERL, Cincinnati, OH 45268.

Morris, J. C. and B. Baum. 1978. Precursors and Mechanisms of Haloform Formation in the Chlorination of Water Supplies. In: Water Chlorination: Environmental Impact and health Effect, Vol. 2, ed. R. L. Jolley, H. Gorchev and D. H. Hamilton, Jr. Ann Arbor Science Pub. Inc., Ann Arbor MI p29-48.

- Oliver, B. G. 1980. Water Chlorination, Vol. 3, R. Jolley, et al., eds. Ann Arbor Science, MI. p.141.
- Oliver, B. G.; J. Lawrence. 1979. Haloforms in Drinking Water. A Study of Precursor Removal. J. Am. Water Works Assoc., 71: 161-163.
- Rook, J.J. 1974. Formation of Haloforms During Chlorination of Natural Water. Water Treatment Exam. 23: 234.
- Rook, J. J. 1976. Haloforms in Drinking Water. J. Am. Water Works Assoc. 68: 168.
- Rook, J. J. 1978. Chlorination Reactions of Fulvic Acids in Natural Waters. Environmental Science and Technology 11: 478-482.
- Saunier, B. M. and Selleck, R. E. 1979. The Kinetics of Breakpoint Chlorination in Continuous Flow Systems. J. Am. Water Works Assoc. 71: 164-172.
- Searle, C. E. 1976. Chemical Carcinogens. Monograph 173: American Chemical Society, Washington, D. C.
- Singer, P.C.; J. H. Borchardt; J. M. Colthurst. 1980. The Effects of Permanganate Pretreatment on Trihalomethane Formation in Drinking Water. J. Am. Water Works Assoc. 72: 573-578.
- Singley, E. 1977. Minimizing Trihalomethane Formation in a Softening Plant. Municipal Environmental Research Lab., Off. of Res. and Dev., US EPA, I.C. Report Cincinnati, OH.
- Standard Methods for the Examination of Water and Wastewater, 15th ed., AWWA, APHA, WPCF, 1981.
- Stevens, A. A.; C. J. Slocum; D. R. Seeger; G. G. Robeck. 1976. Chlorination of Organics in Drinking Water. J. Am. Water Works Assoc. 68: 615.
- Stevens, A. A.; J. M. Symons. 1977. Measurement of Trihalomethanes and Precursor Concentration Changes. J. Am. Water Works Assoc. 9: 546.
- Suffet, I. H.; M. J. McGuire. Proceedings of Conference Activated Carbon Adsorption of Organics from the Aqueous Phase, Vols. 1 and 2, Ann Arbor Science Publisher, Inc., Ann Arbor, MI (In Press).
- Symons, J. M.; A. A. Stevens; C. M. Robert; E. E. Geldreich; O. T. Love; J. DeMarco. 1981. Treatment Techniques for Controlling Trihalomethanes in Drinking Water. United States Environmental Protection Agency. Municipal Environmental Research Laboratory Cincinnati, OH 1-23pp.
- Symons, J. M.; T. A. Bellar; J. K. Carswell; J. DeMarco; L. K. Kropp; G. G. Robeck; D. R. Seeger; C. J. Slocum; B. L. Smith; A. A. Stevens. 1975. National Organics Reconnaissance Survey for Halogenated Organics. J. Am. Water Works Assoc. 67: 634

Symons, J. M.; J. K. Carswell; R. M. Clark; P. Dorsey; E. E. Geldreich; P. Hefferman; J. C. Hoff; O. T. Love, Jr.; L. J. McCabe; A. A. Stevens. 1979. Ozone, Chlorine Dioxide and Chloramines as Alternatives to Chlorine for Disinfection of Drinking Water. In: Water Chlorination Environmental Impact and Health Effect, Vol. 2. ed. R. L. Jolley; H. Gorchev; D. H. Hamilton, Ann Arbor Science Publishers, Inc., Ann Arbor, MI., pp 555-560 (1978); also Report of the Water Supply Research, Off. of Res. and Dev. US EPA, Cincinnati, OH. 1977, revised 1978, reprinted (1979).

Trehy, M. L.; T. I. Bieber. 1980. Effect of Commonly Used Water Treatment Processes on the Formation of THM's and DHAN's. Proceedings of the AWWA 1980 Annual Conference, Atlanta, GA. June 15-20, 125-138 pp.

Trussell, R. R. 1978. Factors Influencing the Formation of Trihalomethanes. In: Organics in Domestic Water Supplies, Proceedings, California - Nevada Section Forum, J. Am. Water Works Assoc. Palo Alto, CA (April 12, 1978).

Trussell, R. R.; M. D. Umphres. 1978. The Formation of Trihalomethanes. J. Am. Water Works Assoc. 70: 604-612.

Veenstra, J. N.; J. L. Schnoor. 1980. Seasonal Variations in Trihalomethane Levels in an Iowa River Water Supply. J. Am. Water Works Assoc. 72: 583-590.

Wood, P. R.; D. F. Jackson; J. A. Gervers; D. H. Waddell; L. Kaplan. 1978. Removing Potential Organic Carcinogens and Precursors from Drinking Water. Final Report. Grant No. CR804521-01. Environ. Mon. and Support Lab., US EPA, Cincinnati, OH.

Appendix A

TABLE A-1

TRIHALOMETHANE CONCENTRATION IN CHLORINATED GROUND WATER AS A FUNCTION OF TIME.
(pH = 7; $\text{Cl}_2 = 2.82 \times 10^{-5} \text{ mol/L} = 2.00 \text{ mg/L}$; no Br^- added)

Time Hours	Trihalomethanes										Total					Incorporated	
	CHCl ₃		CHCl ₂ Br		CHClBr ₂		CHBr ₃		THM	THM	Br	Organic Cl	Cl/Br	Br	Cl		
	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	mol/L x 10 ⁻⁹	mol/L x 10 ⁻⁹	mol/L x 10 ⁻⁹				
1	4.20+1.30	35.2+10.9	2.10+1.20	12.8+7.3	1.80+1.30	8.62+6.23	2.10+0.40	8.32+1.58	10.2	64.9	54.9	140	2.55	N.A.	0.496		
2	4.30+0.90	36.0+7.5	2.10+0.15	12.8+0.9	1.80+1.70	8.62+8.14	2.10+0.70	8.32+2.77	10.3	65.7	54.9	142	2.59	N.A.	0.504		
4	4.40+1.40	36.9+11.7	2.20+1.10	13.4+6.7	2.10+1.00	10.1+4.81	2.10+1.10	8.32+4.36	10.8	68.7	58.3	146	2.50	N.A.	0.518		
8	4.40+1.20	36.9+10.1	2.30+1.40	14.0+8.5	2.30+1.10	11.0+5.31	2.10+0.90	8.32+3.56	11.1	70.2	60.9	149	2.45	N.A.	0.528		
24	4.40+1.70	36.9+14.2	2.50+1.30	15.3+7.9	2.30+1.80	11.0+8.6	2.10+0.30	8.32+1.19	11.3	71.5	62.2	152	2.44	N.A.	0.539		
48	4.50+1.80	37.7+15.1	2.50+0.70	15.3+4.3	2.40+1.30	11.5+6.2	2.10+1.20	8.32+4.75	11.5	72.8	63.2	155	2.45	N.A.	0.550		
96	4.50+0.80	37.7+6.7	2.60+1.80	15.9+11.0	2.40+1.30	11.5+6.2	2.20+0.60	8.71+2.38	11.7	73.8	65.0	156	2.40	N.A.	0.553		
144	4.50+1.40	37.7+11.7	2.70+1.10	16.5+6.7	2.60+0.90	12.5+4.3	2.20+0.40	8.71+1.58	12.0	75.4	67.6	158	2.34	N.A.	0.560		

*Not Applicable

TABLE A-2

TRIHALOMETHANE CONCENTRATION IN CHLORINATED GROUND WATER AS A FUNCTION OF TIME.
(pH = 7; Cl₂ = 11.3 × 10⁻⁵ mol/L = 8.00 mg/L; no Br⁻ added)

Time	Trihalomethanes										Total				Incorporated	
	CHCl ₃		CHCl ₂ Br		CHClBr ₂		CHBr ₃		THM	THM	Organic		Br	Cl		
	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹			Br	Cl			Cl/Br	
Hours																
1	4.40±0.30	36.9±2.5	2.40±1.10	14.6±6.7	2.00±0.60	9.58±2.9	2.20±2.10	8.71±8.32	11.0	69.8	59.9	150	2.50	N.A.*	0.133	
2	4.60±1.30	38.5±10.9	2.50±1.30	15.3±7.9	2.20±1.20	10.5±5.8	2.30±1.80	9.11±7.13	11.6	73.4	63.6	157	2.47	N.A.	0.140	
4	4.80±1.20	40.2±10.1	2.50±1.10	15.3±6.7	2.40±1.30	11.5±6.2	2.30±1.30	9.11±5.15	12.0	76.1	65.6	163	2.48	N.A.	0.144	
8	5.10±0.50	42.7±42	2.60±1.20	15.9±7.3	2.50±1.11	12.0±5.3	2.40±1.70	9.50±6.73	12.6	80.1	68.4	172	2.51	N.A.	0.152	
24	5.30±1.10	44.4±9.2	2.80±0.80	17.1±4.9	2.60±1.40	12.5±6.7	2.40±1.90	9.50±7.52	13.1	83.5	70.5	180	2.55	N.A.	0.159	
48	6.10±0.70	51.1±5.9	2.90±1.35	17.7±8.2	2.70±0.90	12.9±4.3	2.40±1.50	9.50±5.94	14.1	91.2	72.0	202	2.81	N.A.	0.179	
96	6.30±1.60	52.6±13.4	3.10±1.60	18.9±9.8	2.80±0.80	13.4±3.8	2.40±1.40	9.50±5.54	14.6	94.6	74.2	210	2.83	N.A.	0.186	
144	6.50±1.30	54.5±10.9	3.30±1.50	20.1±9.2	2.90±0.40	13.9±2.0	2.50±1.40	9.90±5.54	15.2	98.4	77.6	218	2.81	N.A.	0.193	

Not Applicable

*Not Applicable

TABLE A-3
 TRIHALOMETHANE CONCENTRATION IN CHLORINATED GROUND WATER AS A FUNCTION OF TIME.
 (pH = 7; $\text{Cl}_2 = 16.9 \times 10^{-5} \text{ mol/L} = 12.0 \text{ mg/L}$, no Br^- added)

Time	Trihalomethanes										Total					Incorporated	
	CHCl ₃		CHCl ₂ Br		CHClBr ₂		CHBr ₃		THM	THM	Br mol/L x 10 ⁻⁹	Organic Cl		Br	Cl		
	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹		Cl/Br					
1	12.1±2.5	101±21	3.00±0.90	18.3±5.5	3.10±0.30	14.8±1.4	2.20±1.70	8.71±6.73	20.4	143	74.0	354	4.78	N.A.*	0.210		
2	12.3±1.4	103±12	3.30±1.70	20.1±10.4	3.30±0.80	15.8±3.8	2.30±1.50	9.11±5.94	21.2	148	79.0	365	4.62	N.A.	0.216		
4	13.7±1.6	115±13	3.50±1.60	21.4±3.7	3.40±1.10	16.2±5.3	2.40±1.20	9.50±4.75	23.0	162	82.3	404	4.91	N.A.	0.239		
8	14.9±1.2	125±10	3.80±0.40	23.2±2.4	3.70±1.15	17.7±5.5	2.70±0.80	10.7±3.12	25.1	177	90.7	439	4.84	N.A.	0.260		
24	15.6±1.8	131±15	4.10±1.30	25.0±7.9	3.80±0.95	18.2±4.6	2.70±0.95	10.7±3.8	26.2	185	93.5	461	4.93	N.A.	0.272		
48	17.3±2.3	145±19	4.30±0.80	26.2±4.9	3.90±1.80	18.7±8.6	2.80±1.30	11.1±5.2	28.3	201	96.6	506	5.24	N.A.	0.299		
96	18.6±1.8	156±15	4.50±1.10	27.5±6.7	4.00±1.50	19.2±7.2	2.90±2.10	11.5±8.3	30.0	214	100	542	5.42	N.A.	0.321		
144	21.2±1.9	178±16	4.60±0.50	28.1±3.1	4.20±1.60	20.1±7.7	3.30±1.80	13.1±7.1	33.3	239	107	610	5.70	N.A.	0.361		
Not Applicable																	

*Not Applicable

TABLE A-4

TRIHALOMETHANE CONCENTRATION IN CHLORINATED GROUND WATER AS A FUNCTION OF TIME.
(pH = 7; $\text{Cl}_2 = 22.6 \times 10^{-5} \text{ mol/L} = 16.0 \text{ mg/L}$; no Br^- added)

Time	Trihalomethanes										Total					Incorporated	
	CHCl ₃		CHCl ₂ Br		CHClBr ₂		CHBr ₃		THM	THM	Br	Organic Cl	Cl/Br	Br	Cl		
	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	mol/L x 10 ⁻⁹	mol/L x 10 ⁻⁹	mol/L x 10 ⁻⁹				
Hours																	
1	4.90±1.10	41.1±9.2	2.60±1.40	15.9±8.5	2.20±1.10	10.5±5.3	2.20±1.30	8.71±5.15	11.9	76.2	63.0	165	2.62	N.A.	0.073		
2	5.40±2.60	45.3±21.8	2.80±1.20	17.1±7.3	2.30±0.95	11.0±4.6	2.30±0.80	9.11±3.17	12.8	82.5	66.3	181	2.73	N.A.	0.080		
4	6.10±1.10	51.1±9.2	2.90±1.50	17.7±9.2	2.50±1.30	12.0±6.2	2.30±2.10	9.11±8.32	13.8	89.9	69.0	201	2.91	N.A.	0.089		
8	6.90±1.30	57.8±10.9	3.10±1.30	18.9±7.9	2.70±0.90	12.9±4.3	2.40±0.40	9.50±1.58	15.1	99.1	73.4	224	3.05	N.A.	0.099		
24	7.20±1.40	60.3±11.7	3.30±1.80	20.1±11.0	2.70±1.80	12.9±8.6	2.40±0.50	9.50±1.98	15.6	103	74.6	234	3.14	N.A.	0.104		
48	7.90±1.30	66.2±10.9	3.40±0.70	20.7±4.3	2.80±1.40	13.4±6.7	2.50±1.20	9.90±4.75	16.6	110	77.2	253	3.28	N.A.	0.112		
96	8.30±1.50	70.0±12.6	3.80±1.60	23.2±9.8	2.90±0.50	13.9±2.4	2.50±1.40	9.90±5.54	17.5	117	80.7	270	3.35	N.A.	0.119		
144	8.90±2.40	74.6±20.1	4.20±2.50	25.6±15.3	3.10±1.50	14.8±7.2	2.50±1.60	9.90±6.34	18.7	124	84.9	288	3.39	N.A.	0.127		

*Not Applicable

TABLE A-5
 TRIHALOMETHANE CONCENTRATION IN CHLORINATED GROUND WATER AS A FUNCTION OF TIME.
 (pH = 7; Cl₂ = 33.8 x 10⁻⁵ mol/L = 24.0 mg/L; no Br⁻ added)

Time	Trihalomethanes										Total				Incorporated	
	CHCl ₃		CHCl ₂ Br		CHClBr ₂		CHBr ₃		THM	THM	THM	Br	Organic		Br	Cl
	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹					Br	Cl		
1	45.0±8.30	377±70	24.0±5.1	146±31	13.4±2.5	64.2±12.0	4.00±1.50	15.8±5.9	86.4	603	322	1490	4.63	N.A.	0.441	
2	54.0±21.0	453±176	28.0±4.3	171±26	16.8±5.5	80.5±26.3	4.00±1.10	15.8±4.4	103	720	380	1780	4.68	N.A.	0.527	
4	77.0±10.5	645±88	34.0±2.2	207±13	22.5±6.1	108±29	4.30±3.80	17.0±15.0	138	977	474	2460	5.19	N.A.	0.728	
8	80.0±13.1	670±110	41.0±10.7	250±65	34.1±9.5	163±46	4.50±1.20	17.8±4.8	160	1100	630	2670	4.24	N.A.	0.790	
24	83.0±17.7	696±148	52.0±6.5	317±40	37.2±7.1	178±34	4.50±2.70	17.8±10.7	177	1210	726	2900	3.99	N.A.	0.858	
48	85.0±14.3	712±120	59.0±7.2	360±44	38.0±5.5	182±26	4.70±1.30	18.6±5.2	187	1270	780	3040	3.90	N.A.	0.899	
96	90.0±12.1	754±101	63.0±8.7	384±53	38.4±3.2	184±15	4.70±1.80	18.6±7.1	196	1340	808	3210	3.97	N.A.	0.950	
144	95.0±5.5	796±46	65.0±9.3	397±57	38.9±4.5	186±22	4.80±2.10	19.0±8.3	204	1400	826	3370	4.08	N.A.	0.997	

*Not Applicable

TABLE A-6
 TRIHALOMETHANE CONCENTRATION IN CHLORINATED GROUND WATER AS A FUNCTION OF TIME.
 (pH = 7; Cl₂ = 50.8 x 10⁻⁵ mol/L = 36.0 mg/L; no Br⁻ added)

Time	Trihalomethanes						Total					Incorporated	
	CHCl ₃		CHCl ₂ Br		CHClBr ₂		CHBr ₃		THM	THM	Organic		Cl
	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	Br	Cl	
Hours													
1	63.0±7.3	528±61	46.3±18.0	282±110	19.9±1.9	95.3±9.1	4.50±1.10	17.8±4.4	134	923	525	2240	N.A.* 0.441
2	74.0±5.2	620±43	65.4±14.0	399±85	25.1±2.7	120±13	4.50±2.50	17.8±9.9	169	1160	692	2780	N.A. 0.547
4	88.0±6.3	737±53	71.0±19.5	433±119	27.0±2.1	129±10	4.80±1.70	19.0±6.7	191	1320	748	3200	N.A. 0.630
8	110±16	922±134	79.3±4.1	484±25	32.1±1.8	154±9	4.80±1.70	19.0±2.8	226	1580	849	3890	N.A. 0.766
24	130±9	1090±71	82.0±3.2	500±20	33.2±1.1	159±5	4.80±1.30	19.0±5.2	250	1770	875	4430	N.A. 0.872
48	140±12	1170±101	83.0±12.1	506±74	38.1±7.0	182±34	5.10±2.20	20.1±8.7	266	1880	930	4700	N.A. 0.925
96	224±19	1880±159	89.0±18.0	543±110	39.6±1.6	190±8	5.10±2.80	20.1±11.1	358	2630	983	6920	N.A. 1.36
144	262±29	2220±243	106±17	647±104	40.9±2.0	196±10	5.30±1.90	21.0±7.5	414	3080	1100	8150	N.A. 1.60

*Not Applicable

TABLE A-7

TRIHALOMETHANE CONCENTRATION IN CHLORINATED GRUND WATER AS A FUNCTION OF TIME.
(pH = 9; Cl₂ = 2.82×10^{-5} mol/L = 2.00 mg/L; no Br⁻ added)

Time	Trihalomethanes										Total				Incorporated	
	CHCl ₃		CHCl ₂ Br		CHClBr ₂		CHBr ₃		THM	THM	THM	Br ⁻	Organic Cl	Cl/Br	Br	Cl
	ug/L	mol/L $\times 10^{-9}$	ug/L	mol/L $\times 10^{-9}$	ug/L	mol/L $\times 10^{-9}$	ug/L	mol/L $\times 10^{-9}$	ug/L	ug/L	mol/L $\times 10^{-9}$	mol/L $\times 10^{-9}$	mol/L $\times 10^{-9}$			
1	4.40±1.10	36.9±9.2	2.20±0.10	13.4±0.6	1.80±1.00	8.62±4.79	2.00±0.20	7.92±0.79	10.4	66.8	54.3	146	2.69		N.A.*	0.518
2	4.40±0.10	36.9±0.8	2.20±0.29	13.4±1.8	1.80±0.50	8.62±2.40	2.10±1.10	8.32±4.36	10.5	67.2	55.5	146	2.63		N.A.	0.518
4	4.40±1.80	36.9±15.1	2.20±1.05	13.4±6.4	2.00±1.10	9.58±5.27	2.10±0.30	8.32±1.19	10.7	68.2	58.0	147	2.53		N.A.	0.521
8	4.50±2.10	37.7±17.6	2.20±1.50	13.4±9.2	2.10±0.80	10.1±3.8	2.20±0.20	8.71±0.79	11.0	69.8	63.1	157	2.49		N.A.	0.557
24	4.50±1.10	37.7±9.2	2.80±1.20	17.1±7.3	2.20±0.10	10.5±0.5	2.30±0.60	9.11±2.38	11.8	74.4	65.4	158	2.42		N.A.	0.560
48	4.50±2.10	37.7±17.6	2.80±1.10	17.1±6.7	2.20±1.00	10.5±4.8	2.30±0.51	9.11±2.02	11.8	74.4	65.4	158	2.42		N.A.	0.560
96	4.50±1.10	37.7±9.2	2.80±0.50	17.1±3.1	2.40±1.20	11.5±5.8	2.40±1.20	9.50±4.75	12.1	75.8	68.6	159	2.32		N.A.	0.563
144	4.70±2.10	39.4±17.6	2.80±0.70	17.1±4.3	2.60±1.50	12.5±7.2	2.40±0.50	9.50±1.98	12.5	78.5	70.6	165	2.34		N.A.	0.585

*Not Applicable

TABLE A-8
 TRIHALOMETHANE CONCENTRATION IN CHLORINATED GROUND WATER AS A FUNCTION OF TIME.
 (pH = 9; Cl₂ = 11.3×10^{-5} mol/L = 8.00 mg/L; no Br⁻ added)

Time Hours	Trihalomethanes										Total					Incorporated	
	CHCl ₃		CHCl ₂ Br		CHClBr ₂		CHBr ₃		THM ug/L	THM mol/L x 10 ⁻⁹	Organic			Br	Cl		
	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹			Br	Cl	Cl/Br				
1	4.50±1.80	37.1±15.1	2.60±1.90	15.7±11.6	2.30±1.20	11.0±5.8	2.20±1.40	8.71±5.54	11.6	72.5	63.8	154	2.41	N.A.*	0.136		
2	4.60±0.30	38.5±2.5	2.90±2.00	17.7±12.2	2.40±1.40	11.5±6.7	2.40±0.40	9.50±1.58	12.3	77.2	69.2	162	2.34	N.A.	0.143		
4	6.00±1.10	50.3±9.2	3.10±1.80	18.9±11.0	2.71±0.80	13.0±3.8	2.70±1.60	10.7±6.3	14.5	92.9	77.0	202	2.62	N.A.	0.179		
8	6.80±0.10	60.0±0.8	3.10±1.11	18.9±6.8	2.71±1.90	13.0±9.1	2.70±1.40	10.7±5.5	15.3	103	77.0	231	3.00	N.A.	0.204		
24	7.47±2.10	62.0±17.6	3.20±2.10	19.5±12.8	2.80±0.20	13.4±1.0	2.70±0.50	10.7±2.0	16.1	106	78.4	238	3.04	N.A.	0.211		
48	7.50±3.10	62.9±26.0	3.20±1.60	19.5±9.8	2.80±1.10	13.4±5.3	2.80±1.10	11.1±4.4	16.3	107	79.3	241	3.04	N.A.	0.213		
96	7.80±1.90	65.4±15.9	3.30±1.20	20.1±7.3	3.20±2.10	15.3±10.1	2.90±1.40	11.5±5.5	17.2	112	85.2	252	2.96	N.A.	0.223		
144	8.10±1.40	67.9±11.7	3.30±2.10	20.1±12.8	3.30±0.40	15.8±1.9	2.90±1.20	11.5±4.8	17.6	115	86.2	260	3.02	N.A.	0.230		
Not Applicable																	

*Not Applicable

TABLE A-9
TRIHALOMETHANE CONCENTRATION IN CHLORINATED GROUND WATER AS A FUNCTION OF TIME.
(pH = 9; Cl₂ = 16.9 x 10⁻⁵ mol/L = 12.0 mg/L; no Br⁻ added)

Time Hours	Trihalomethanes										Total				Incorporated	
	CHCl ₃		CHCl ₂ Br		CHClBr ₂		CHBr ₃		THM ug/L	THM mol/L x 10 ⁻⁹	THM mol/L x 10 ⁻⁹	Br mol/L x 10 ⁻⁹	Organic Cl		Br	Cl
	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹					Br	Cl		
1	11.6±1.5	97.2±12.6	3.30±1.50	20.1±9.2	3.30±0.20	15.8±1.0	2.30±1.20	9.10±4.8	20.5	142	79	348	4.41	N.A.*	0.206	
2	12.6±0.5	105±4	3.80±1.60	23.2±9.8	3.30±1.30	15.8±6.2	2.30±0.40	9.10±1.58	22.0	153	82.1	377	4.59	N.A.	0.223	
4	14.4±2.0	121±17	3.80±0.60	23.2±3.7	3.30±1.10	15.8±5.3	3.10±4.10	12.3±16.2	24.6	172	91.7	425	4.63	N.A.	0.251	
8	14.5±1.2	122±10	3.90±1.10	23.8±6.7	3.40±0.10	16.3±0.5	3.10±3.20	12.3±12.7	24.9	174	93.3	430	4.61	N.A.	0.254	
24	17.3±3.1	145±26	4.00±0.20	24.4±1.2	3.50±1.10	16.8±5.3	3.20±0.10	12.7±0.4	28.0	199	96.1	501	5.21	N.A.	0.296	
48	18.3±2.9	153±24	4.10±0.10	25.0±0.6	3.50±0.80	16.8±3.8	3.20±4.10	12.7±16.2	29.1	208	96.7	526	5.44	N.A.	0.311	
96	20.2±5.4	169±45	5.00±0.20	30.5±1.2	3.70±2.10	17.7±10.1	3.30±1.10	13.1±4.4	32.2	230	105	586	5.58	N.A.	0.347	
144	22.0±4.5	184±38	5.20±3.10	31.8±18.9	3.80±0.30	18.2±1.4	3.40±0.40	13.5±1.6	34.4	248	109	633	5.81	N.A.	0.375	

*Not Applicable

TABLE A-10
TRIHALOMETHANE CONCENTRATION IN CHLORINATED GROUND WATER AS A FUNCTION OF TIME.
(pH = 9; $\text{Cl}_2 = 22.6 \times 10^{-5} \text{ mol/L} = 16.0 \text{ mg/L}$; no Br^- added)

Time		Trihalomethanes										Total					Incorporated	
Hours	CHCl ₃		CHCl ₂ Br		CHClBr ₂		CHBr ₃		THM ug/L	THM mol/L x 10 ⁻⁹	THM mol/L x 10 ⁻⁹	Organic			Br	Cl		
	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹				Br mol/L x 10 ⁻⁹	Cl mol/L x 10 ⁻⁹	Cl/Br				
1	4.90±1.00	41.1±8.4	2.50±0.20	15.3±1.2	2.30±1.10	11.0±5.3	2.40±0.50	9.50±1.98	12.1	76.9	65.8	165	2.51	N.A.*	0.073			
2	5.90±1.90	49.4±15.9	2.50±0.10	15.3±0.6	2.30±1.30	11.0±6.2	2.40±1.10	9.50±4.37	13.1	85.2	65.8	190	2.89	N.A.	0.084			
4	6.50±0.10	54.5±0.8	2.50±1.70	15.3±10.8	2.40±0.80	11.5±3.8	2.40±0.10	9.50±0.40	13.8	90.8	66.8	206	3.08	N.A.	0.091			
8	7.10±3.20	59.5±26.8	2.60±0.20	15.9±1.2	2.40±0.40	11.5±1.9	2.50±0.30	9.90±1.20	14.6	96.8	68.6	206	3.00	N.A.	0.091			
24	7.80±2.60	65.4±21.8	2.70±1.00	16.5±6.1	2.50±1.80	12.0±8.6	2.50±1.20	9.90±4.75	15.5	104	70.2	241	3.43	N.A.	0.107			
48	8.40±0.40	70.4±3.5	3.20±0.10	19.5±0.6	2.60±1.10	12.5±5.3	2.50±0.70	9.90±2.80	16.7	112	74.2	263	3.54	N.A.	0.116			
96	9.10±1.10	76.3±9.2	3.60±1.30	22.0±7.9	2.80±0.50	13.4±2.4	2.60±0.90	10.3±3.6	18.1	122	79.7	286	3.59	N.A.	0.127			
144	10.2±2.10	85.5±17.6	4.50±1.40	27.5±8.5	2.80±0.70	13.4±3.4	2.60±0.80	10.3±3.2	20.1	137	85.2	325	3.81	N.A.	0.144			

*Not Applicable

TABLE A-11
 TRIHALOMETHANE CONCENTRATION IN CHLORINATED GROUND WATER AS A FUNCTION OF TIME.
 (pH = 9; Cl₂ = 33.8 x 10⁻⁵ mol/L = 24.0 mg/L; no Br⁻ added)

Time	Trihalomethanes										Total				Incorporated	
	CHCl ₃		CHCl ₂ Br		CHClBr ₂		CHBr ₃		THM ug/L	THM mol/L x 10 ⁻⁹	THM mol/L x 10 ⁻⁹	Br ⁻ mol/L x 10 ⁻⁹	Organic Cl ⁻ mol/L x 10 ⁻⁹	Cl/Br	Br	Cl
	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹								
1	59.0±3.0	494±25	28.0±4.0	171±24	15.0±3.0	71.9±14.4	3.50±0.10	13.9±0.4	106	751	356	1900	5.34	N.A.*	0.562	
2	68.0±6.0	570±50	32.0±12.0	195±73	25.0±4.0	120±19	3.60±0.70	14.3±2.8	129	899	478	2200	4.60	N.A.	0.651	
4	81.0±10.0	679±84	38.0±1.2	232±7	33.0±19.0	158±91	4.30±1.80	17.0±7.1	156	1090	599	2660	4.44	N.A.	0.787	
8	88.0±3.0	737±25	55.0±10.0	336±61	37.0±5.0	177±24	4.30±1.10	17.0±4.4	184	1270	741	3060	4.13	N.A.	0.905	
24	91.0±10.0	763±84	56.0±3.0	342±18	37.0±5.2	177±25	4.30±1.20	17.0±4.8	188	1300	747	3150	4.22	N.A.	0.932	
48	92.0±11.0	771±92	57.0±10.0	348±61	38.0±6.1	182±29	4.60±0.80	18.2±3.2	192	1320	766	3190	4.16	N.A.	0.944	
96	94.0±2.0	787±17	62.0±5.0	378±31	41.0±4.2	196±20	4.60±0.50	18.2±2.0	202	1380	826	3310	4.01	N.A.	0.979	
144	96.0±10.0	804±84	63.0±6.0	384±37	46.0±4.0	220±19	4.80±1.10	19.0±4.4	210	1430	881	3400	3.86	N.A.	1.01	

*Not Applicable

TABLE A-12

TRICHALOMETHANE CONCENTRATION IN CHLORINATED GROUND WATER AS A FUNCTION OF TIME.
(pH = 9; Cl₂ = 50.8 x 10⁻⁵ mol/L = 36.0 mg/L; no Br⁻ added)

Time Hours	Trihalomethanes										Total				Incorporated	
	CHCl ₃		CHCl ₂ Br		CHClBr ₂		CHBr ₃		THM ug/L	THM mol/L x 10 ⁻⁹	THM mol/L x 10 ⁻⁹	Br mol/L x 10 ⁻⁹	Organic Cl		Br	Cl
	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹					Br	Cl		
1	69.0±6.0	578±50	63.0±17.0	384±104	22.0±5.0	105±24	4.80±1.10	19.0±4.4	159	1090	657	2610	3.97		N.A.*	0.514
2	84.0±8.3	704±70	68.0±5.2	415±32	31.0±12.0	149±58	4.80±0.61	19.0±2.4	188	1290	770	3090	4.01		N.A.	0.608
4	98.0±4.0	821±34	72.0±1.2	439±7.3	36.0±5.0	172±24	4.80±0.50	19.0±2.0	211	1450	840	3510	4.18		N.A.	0.691
8	120±12	1010±101	78.0±0.6	476±4	41.0±9.4	196±45	4.90±1.10	19.4±4.4	244	1700	926	4170	4.50		N.A.	0.821
24	160±18	1340±151	84.0±5.0	512±31	45.0±10.1	216±48	4.90±1.10	19.4±4.4	294	2090	1000	5260	5.26		N.A.	1.04
48	185±14	1550±117	85.0±4.6	519±28	46.0±2.0	220±10	5.10±1.30	20.2±5.2	321	2310	1020	5910	5.79		N.A.	1.16
96	229±25	1920±210	88.0±3.2	537±20	47.0±4.1	225±20	5.40±0.40	20.2±1.6	369	2700	1050	7050	6.71		N.A.	1.39
144	279±18	2340±149	103±27	628±165	51.0±2.3	244±11	5.80±0.10	23.0±0.4	439	3240	1190	8520	7.16		N.A.	1.68

*Not Applicable

Appendix B
TABLE B-1

TRICHALOMETHANE CONCENTRATION IN CHLORINATED GROUND WATER AS A FUNCTION OF TIME.
(pH = 7; Cl₂ = 2.82 x 10⁻⁵ mol/L = 2.00 mg/L; Br⁻ = 1 x 10⁻⁶ mol/L)

Time	Trihalomethanes										Total					Incorporated	
	CHCl ₃		CHCl ₂ Br		CHClBr ₂		CHBr ₃		THM	THM	Organic			Br	Cl		
	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	Br mol/L x 10 ⁻⁹	Cl mol/L x 10 ⁻⁹	Cl/Br				
Hours																	
1	2.29±0.24	19.2±2.0	1.93±0.55	11.8±3.4	1.65±0.18	7.90±0.86	1.21±1.15	4.79±4.55	7.08	43.7	42.0	89.1	2.12	4.20	0.316		
2	2.33±0.13	19.5±1.1	1.94±1.21	11.8±7.4	1.67±0.19	8.00±0.91	1.22±2.11	4.83±8.36	7.16	44.1	42.3	90.1	2.13	4.23	0.320		
4	2.58±1.05	21.6±8.8	1.99±0.13	12.1±0.8	1.93±1.11	9.24±5.32	1.57±1.25	6.22±4.95	8.07	49.2	49.2	98.2	2.00	4.92	0.348		
8	2.75±0.13	23.0±1.1	2.15±0.51	13.1±3.1	2.11±0.34	10.1±1.6	1.65±0.99	6.53±3.92	8.66	52.7	52.9	105	1.98	5.29	0.372		
24	3.13±1.88	26.2±15.8	2.28±1.13	13.9±6.9	2.45±0.98	11.7±4.7	1.95±1.81	7.72±7.17	9.81	59.5	60.5	118	1.95	6.05	0.418		
48	3.55±1.18	29.7±9.9	2.45±1.31	14.9±8.0	2.59±1.15	12.4±5.5	2.26±1.18	8.95±4.67	10.9	66.0	66.6	131	1.97	6.66	0.465		
96	3.98±1.15	33.4±9.6	2.66±1.11	16.2±6.8	2.64±1.05	12.6±5.0	2.45±0.95	9.70±3.76	11.7	71.9	70.5	145	2.06	7.05	0.514		
144	4.14±1.09	34.7±9.1	2.88±0.59	17.7±3.6	2.68±2.01	12.8±9.6	2.55±1.18	10.1±4.7	12.3	75.3	73.6	152	2.07	7.36	0.539		

TABLE B-2

TRICHALOMETHANE CONCENTRATION IN CHLORINATED GROUND WATER AS A FUNCTION OF TIME.
(pH = 7; $\text{Cl}_2 = 8.46 \times 10^{-5} \text{ mol/L}$; $\text{Br}^- = 1 \times 10^{-6} \text{ mol/L}$)

Time Hours	Trihalomethanes										Total				Incorporated	
	CHCl ₃		CHCl ₂ Br		CHClBr ₂		CHBr ₃		THM	THM	THM $\text{mol/L} \times 10^{-9}$	Organic			Br	Cl
	$\mu\text{g/L}$	$\text{mol/L} \times 10^{-9}$	$\mu\text{g/L}$	$\text{mol/L} \times 10^{-9}$	$\mu\text{g/L}$	$\text{mol/L} \times 10^{-9}$	$\mu\text{g/L}$	$\text{mol/L} \times 10^{-9}$	$\mu\text{g/L}$	$\text{mol/L} \times 10^{-9}$		Br	Cl	Cl/Br		
1	6.15 $\pm$ 3.17	51.5 $\pm$ 26.6	4.60 $\pm$ 2.31	28.0 $\pm$ 14.1	2.11 $\pm$ 1.22	10.1 $\pm$ 5.8	2.10 $\pm$ 1.13	8.32 $\pm$ 4.47	15.0	97.9	73.2	221		3.02	9.79	0.261
2	6.29 $\pm$ 0.58	52.7 $\pm$ 4.9	4.66 $\pm$ 0.34	28.4 $\pm$ 2.1	2.38 $\pm$ 0.14	11.4 $\pm$ 0.7	2.29 $\pm$ 0.58	9.07 $\pm$ 2.30	15.6	102	78.4	226		2.88	10.2	0.267
4	6.33 $\pm$ 2.44	53.0 $\pm$ 20.4	4.78 $\pm$ 1.19	29.2 $\pm$ 7.3	2.51 $\pm$ 0.55	12.0 $\pm$ 2.6	2.48 $\pm$ 1.23	9.82 $\pm$ 4.87	16.1	104	82.7	230		2.78	10.4	0.271
8	6.53 $\pm$ 1.18	54.7 $\pm$ 9.9	5.25 $\pm$ 2.12	32.0 $\pm$ 12.9	2.81 $\pm$ 0.19	13.5 $\pm$ 0.9	2.69 $\pm$ 1.98	10.7 $\pm$ 7.8	17.3	111	91.1	242		2.66	11.1	0.286
24	6.79 $\pm$ 2.15	56.9 $\pm$ 18.0	5.55 $\pm$ 1.11	33.9 $\pm$ 6.8	2.99 $\pm$ 2.09	14.3 $\pm$ 10.0	2.79 $\pm$ 0.98	11.0 $\pm$ 3.9	18.1	116	95.5	253		2.65	11.6	0.299
48	7.22 $\pm$ 3.19	60.5 $\pm$ 26.7	5.99 $\pm$ 3.13	36.5 $\pm$ 19.0	3.12 $\pm$ 1.11	14.9 $\pm$ 5.3	3.09 $\pm$ 1.14	12.2 $\pm$ 4.5	19.4	124	103	269		2.61	12.4	0.318
96	7.55 $\pm$ 2.19	63.3 $\pm$ 18.4	6.43 $\pm$ 2.25	39.2 $\pm$ 13.7	3.21 $\pm$ 0.11	15.4 $\pm$ 0.5	3.18 $\pm$ 2.19	12.6 $\pm$ 8.7	20.4	131	108	284		2.63	13.1	0.336
144	7.99 $\pm$ 1.18	67.0 $\pm$ 9.9	6.66 $\pm$ 0.78	40.6 $\pm$ 4.8	3.43 $\pm$ 1.05	16.4 $\pm$ 5.0	3.39 $\pm$ 1.18	13.4 $\pm$ 4.7	21.5	137	114	299		2.62	13.7	0.353

TABLE B-3
 TRIHALOMETHANE CONCENTRATION IN CHLORINATED GROUND WATER AS A FUNCTION OF TIME.
 (pH = 7; $\text{Cl}_2 = 16.9 \times 10^{-5} \text{ mol/L}$; $\text{Br}^- = 1 \times 10^{-6} \text{ mol/L}$)

Time	Trihalomethanes										Total					Incorporated	
	CHCl ₃		CHCl ₂ Br		CHClBr ₂		CHBr ₃		THM ug/L	THM mol/L x 10 ⁻⁹	Organic			Br	Cl		
	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	Br	Cl			Cl/Br						
1	16.7±5.0	140±42	14.8±6.0	90.3±36.8	5.22±1.25	25.0±6.0	5.18±2.09	20.5±8.3	41.9	276	202	626	3.10	20.2	0.370		
2	18.9±2.1	158±18	15.2±8.3	92.7±50.8	5.39±2.12	25.8±10.2	5.25±2.15	20.8±8.5	44.7	297	207	685	3.31	20.7	0.405		
4	19.8±3.2	166±27	15.8±2.2	96.4±13.4	5.78±1.98	27.7±9.5	5.44±1.17	21.5±4.6	46.8	312	216	719	3.33	21.6	0.425		
8	21.4±6.5	179±55	16.9±4.4	103±27	6.13±4.15	29.4±19.9	5.95±2.15	23.6±8.5	50.4	335	233	772	3.31	23.3	0.457		
24	22.6±7.1	189±60	17.5±5.0	107±31	6.44±3.13	30.8±15.0	6.18±2.15	24.5±8.5	52.7	351	242	812	3.36	24.2	0.480		
48	23.8±5.9	199±49	18.8±3.2	115±20	7.14±2.98	34.2±14.3	6.59±3.09	26.1±12.2	56.3	374	262	861	3.29	26.2	0.509		
96	24.9±8.1	209±68	20.3±4.2	124±25	8.22±3.31	39.4±15.9	7.18±3.29	28.4±13.0	60.6	401	288	914	3.17	28.8	0.541		
144	25.7±4.1	215±35	22.4±7.3	137±45	8.44±2.08	40.4±10.0	7.99±0.95	31.6±3.8	64.5	424	313	959	3.06	31.3	0.567		

TABLE B-5
TRIHALOMETHANE CONCENTRATION IN CHLORINATED GROUND WATER AS A FUNCTION OF TIME.
(pH = 7; $\text{Cl}_2 = 33.3 \times 10^{-5} = 23.6 \text{ mg/L}$; $\text{Br}^- = 1 \times 10^{-6} \text{ mol/L}$)

Time	Trihalomethanes										Total					Incorporated	
	CHCl ₃		CHCl ₂ Br		CHClBr ₂		CHBr ₃		THM ug/L	THM mol/L x 10 ⁻⁹	Organic			Br	Cl		
	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹			Br	Cl	Cl/Br				
Hours																	
1	42.9+14.8	360+124	29.3+15.2	179+93	17.3+8.5	82.9+40.8	11.9+4.4	47.1+17.5	101	669	486	1520			3.13	48.6	0.456
2	48.9+10.0	410+84	34.6+6.0	211+36	18.8+13.5	90.1+64.7	12.9+1.2	51.2+4.6	115	762	545	1740			3.19	54.5	0.523
4	58.0+6.0	486+50	41.5+15.8	253+96	24.7+11.5	118+55	14.2+9.0	56.2+35.4	138	913	658	2080			3.16	65.8	0.625
8	78.2+25.1	655+210	52.7+8.8	321+54	28.5+14.1	137+68	17.8+5.6	70.5+22.0	177	1180	807	2740			3.40	80.7	0.823
24	117+45	980+878	68.5+15.9	418+97	32.3+8.9	155+43	19.9+5.1	78.8+20.2	238	1630	964	3930			4.08	96.4	1.18
48	149+25	1250+209	85.3+19.5	520+119	44.2+15.5	212+74	20.5+7.0	81.2+27.5	299	2060	1190	5000			4.20	119	1.50
96	175+24	1470+200	84.5+25.0	515+153	48.3+13.2	231+63	21.3+6.0	84.3+23.6	329	2300	1230	5670			4.61	123	1.70
144	198+12	1660+96	91.4+13.1	558+80	50.1+14.9	240+71	22.1+13.0	87.5+51.5	362	2540	1300	6340			4.88	130	1.90

TABLE B-6
 TRIHALOMETHANE CONCENTRATION IN CHLORINATED GROUND WATER AS A FUNCTION OF TIME.
 (pH = 7; $\text{Cl}_2 = 49.9 \times 10^{-5} \text{ mol/L}$; $\text{Br}^- = 1 \times 10^{-6} \text{ mol/L}$)

Time	Trihalomethanes										Total				Incorporated	
	Hours	CHCl ₃		CHCl ₂ Br		CHClBr ₂		CHBr ₃		THM	THM	Organic			Br	Cl
		ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹			Br	Cl	Cl/Br		
	1	55.2+13.4	463+112	31.4+11.9	192+73	21.9+5.2	105+25	14.5+5.9	57.4+23.3	123	817	574	1880	3.28	57.4	0.377
	2	66.3+19.4	556+163	37.3+13.8	228+84	22.5+11.3	108+54	15.3+3.1	60.6+12.4	141	953	625	2230	3.57	62.5	0.447
	4	80.2+25.9	672+217	48.4+15.8	295+96	23.7+4.5	114+21	16.8+1.2	66.5+4.7	169	1150	720	2270	3.15	72.0	0.454
	8	91.8+32.1	769+269	55.1+18.9	336+115	29.5+5.2	141+25	18.2+4.9	72.1+19.5	195	1320	834	3120	3.74	83.4	0.625
	24	156+39	1310+324	76.8+22.5	468+137	37.9+11.5	182+55	19.1+5.0	75.6+19.9	290	2040	1060	5050	4.76	106	1.01
	48	188+34	1570+281	85.1+11.8	519+72	40.2+17.8	193+85	19.9+7.1	78.8+28.2	333	2360	1140	5940	5.21	114	1.19
	96	230+45	1930+373	96.8+33.1	590+202	44.3+16.9	212+81	20.1+9.0	79.6+35.7	391	2810	1250	7180	5.74	125	1.44
	144	269+52	2250+437	113+28.5	689+174	48.2+25.4	231+122	22.5+5.1	89.1+20.4	453	3260	1420	8360	5.89	142	1.68

TABLE B-7
TRIHALOMETHANE CONCENTRATION IN CHLORINATED GROUND WATER AS A FUNCTION OF TIME.
(pH = 9; $\text{Cl}_2 = 2.82 \times 10^{-5} \text{ mol/L}$; $\text{Br}^- = 1 \times 10^{-6} \text{ mol/L}$)

Time Hours	Trihalomethanes										Total				Incorporated	
	CHCl ₃		CHCl ₂ Br		CHClBr ₂		CHBr ₃		THM	THM	Organic		Br	Cl	Br	Cl
	ug/L	mol/L $\times 10^{-9}$	ug/L	mol/L $\times 10^{-9}$	ug/L	mol/L $\times 10^{-9}$	ug/L	mol/L $\times 10^{-9}$	ug/L	mol/L $\times 10^{-9}$	Br	Cl	mol/L $\times 10^{-9}$	mol/L $\times 10^{-9}$	mol/L $\times 10^{-9}$	mol/L $\times 10^{-9}$
1	4.08±1.15	34.2±9.6	3.81±1.13	23.2±6.9	2.51±1.08	12.0±5.2	2.11±0.59	8.36±2.34	12.5	77.8	72.3	161			7.23	0.571
2	4.09±1.08	34.3±9.1	3.91±0.26	23.9±1.6	2.52±0.85	12.1±4.1	2.12±1.13	8.40±4.74	12.6	78.7	73.3	163			7.33	0.578
4	4.14±0.69	34.7±5.8	3.98±1.16	24.3±7.1	2.65±0.61	12.7±2.9	2.35±1.18	9.31±4.67	13.1	81.0	77.6	165			7.76	0.585
8	4.51±1.18	37.8±9.9	4.01±0.14	24.5±0.9	2.71±0.54	13.0±2.6	2.61±1.65	10.3±6.5	13.8	85.6	81.4	175			8.14	0.621
24	5.03±2.14	42.2±17.9	4.15±1.15	25.3±7.0	2.79±0.45	13.4±2.2	2.65±0.69	10.5±2.7	14.6	91.4	83.6	191			8.36	0.677
48	6.11±2.07	51.2±17.3	4.31±0.75	26.3±4.6	2.85±0.52	13.5±2.5	2.71±1.18	10.7±4.7	16.0	102	85.4	220			8.54	0.780
96	6.66±1.21	55.8±10.1	4.91±0.53	30.0±3.2	2.93±0.39	14.0±1.9	2.73±0.13	10.8±0.5	17.2	111	90.4	241			9.04	0.855
144	6.98±1.09	58.5±9.1	4.98±1.12	30.4±6.8	2.98±1.03	14.3±4.9	2.85±1.18	11.3±4.7	17.8	115	92.9	251			9.29	0.890

TABLE B-8
TRIHALOMETHANE CONCENTRATION IN CHLORINATED GROUND WATER AS A FUNCTION OF TIME.
(pH = 9; $\text{Cl}_2 = 8.46 \times 10^{-5} \text{ mol/L}$; $\text{Br}^- = 6.00 \text{ mg/L}$; $\text{Br}^- = 1 \times 10^{-6} \text{ mol/L}$)

Time	Trihalomethanes										Total				Incorporated			
	CHCl ₃		CHCl ₂ Br		CHClBr ₂		CHBr ₃		THM ug/L	THM mol/L x 10 ⁻⁹	THM mol/L x 10 ⁻⁹	Organic		Br mol/L x 10 ⁻⁹	Cl/Br	Cl mol/L x 10 ⁻⁹	Br	Cl
	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹										
Hours																		
1	7.03±2.14	58.9±17.9	5.14±2.19	31.4±13.4	3.19±1.14	15.3±5.5	3.01±1.05	11.9±4.2	18.4	118	97.7	255	2.30	9.77	0.301			
2	7.93±1.18	66.5±9.9	5.32±2.41	32.5±14.7	3.24±0.98	15.5±4.7	3.11±1.18	12.3±4.7	19.6	127	100	280	2.80	10.0	0.331			
4	8.24±2.15	69.1±18.0	5.44±1.18	33.2±7.2	3.33±1.12	16.0±5.4	3.23±1.25	12.8±5.0	20.2	131	104	290	2.79	10.4	0.343			
8	8.69±1.13	72.8±9.5	5.64±1.17	34.4±7.1	3.69±0.33	17.7±1.6	3.45±0.59	13.7±23.4	21.5	139	111	305	2.75	11.1	0.361			
24	8.93±2.45	74.8±20.5	5.96±3.11	36.4±19.0	3.99±0.55	19.1±2.6	3.98±1.18	15.8±4.7	22.9	146	122	316	2.59	12.2	0.374			
48	9.12±3.11	76.4±26.1	6.39±0.59	39.0±3.6	4.03±1.81	19.3±8.7	4.01±1.25	15.9±5.0	23.6	151	125	327	2.62	12.5	0.387			
96	9.33±1.15	78.2±9.6	6.86±1.38	42.0±8.4	4.11±0.59	19.7±2.8	4.10±0.81	16.2±3.2	24.4	156	130	338	2.60	13.0	0.400			
144	9.45±3.35	79.2±29.7	6.99±1.01	42.6±6.2	4.25±2.01	20.4±9.6	4.18±1.25	16.6±5.0	24.9	159	133	343	2.58	13.3	0.405			

TABLE B-9
 TRIHALOMETHANE CONCENTRATION IN CHLORINATED GROUND WATER AS A FUNCTION OF TIME.
 (pH = 9; $\text{Cl}_2 = 16.9 \times 10^{-5} \text{ mol/L}$; $\text{Br}^- = 1 \times 10^{-6} \text{ mol/L}$)

Time	Trihalomethanes										Total					Incorporated	
	CHCl ₃		CHCl ₂ Br		CHClBr ₂		CHBr ₃		THM ug/L	THM mol/L x 10 ⁻⁹	THM mol/L x 10 ⁻⁹	Organic			Br	Cl	
	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹				Br	Cl	Cl/Br			
Hours																	
1	39.2±6.93	328±50	18.9±5.2	115±32	6.13±2.15	29.4±10.3	5.95±2.09	23.6±8.3	70.2	496	245	1240	5.06	24.5	0.734		
2	40.1±3.21	336±27	19.5±6.2	119±38	6.21±4.01	29.7±19.2	6.10±3.12	24.2±12.4	71.9	509	251	1280	5.10	25.1	0.757		
4	40.8±11.3	342±95	20.3±7.9	124±48	6.25±3.12	29.9±14.9	6.13±2.15	24.3±8.5	73.5	520	257	1300	5.06	25.7	0.769		
8	42.5±9.15	356±77	20.9±4.3	127±26	6.44±0.59	30.8±2.8	6.29±1.39	24.9±5.5	76.1	539	263	1350	5.13	26.3	0.799		
24	44.3±11.2	371±94	21.4±9.7	131±59	7.03±1.19	33.7±5.7	6.85±2.15	27.1±8.5	79.6	563	280	1410	5.04	28.0	0.834		
48	45.2±8.50	379±71	22.5±4.2	137±26	7.15±4.05	34.3±19.4	6.99±1.99	27.7±7.9	81.8	578	289	1450	5.02	28.9	0.858		
96	47.4±11.1	397±93	25.1±5.2	153±32	7.55±3.22	36.2±15.4	7.15±7.18	28.3±28.4	87.2	615	310	1530	4.94	31.0	0.905		
144	50.2±18.1	421±152	27.8±13.1	170±80	8.01±4.02	38.4±19.3	7.98±5.12	31.6±20.3	94.0	661	342	1640	4.80	34.2	0.970		

TABLE B-10
 TRIHALOMETHANE CONCENTRATION IN CHLORINATED GROUND WATER AS A FUNCTION OF TIME.
 (pH = 9; $\text{Cl}_2 = 22.6 \times 10^{-5} \text{ mol/L} = 16.0 \text{ mg/L}$; $\text{Br}^- = 1 \times 10^{-6} \text{ mol/L}$)

Time Hours	Trihalomethanes										Total				Incorporated	
	CHCl ₃		CHCl ₂ Br		CHClBr ₂		CHBr ₃		THM	THM	Organic		Cl/Br		Br	Cl
	ug/L	mol/L $\times 10^{-9}$	ug/L	mol/L $\times 10^{-9}$	ug/L	mol/L $\times 10^{-9}$	ug/L	mol/L $\times 10^{-9}$	ug/L	mol/L $\times 10^{-9}$	Br	Cl	Br	Cl		
											mol/L $\times 10^{-9}$	mol/L $\times 10^{-9}$				
1	23.5 $\pm$ 7.3	197 $\pm$ 61	15.1 $\pm$ 6.2	92.1 $\pm$ 37.9	5.91 $\pm$ 3.12	28.3 $\pm$ 14.9	4.95 $\pm$ 0.95	19.6 $\pm$ 3.8	49.5	337	208	804	3.87	20.8	0.356	
2	23.8 $\pm$ 7.5	199 $\pm$ 63	15.3 $\pm$ 3.2	93.3 $\pm$ 19.6	6.21 $\pm$ 0.59	29.7 $\pm$ 2.8	5.21 $\pm$ 2.18	20.6 $\pm$ 8.6	50.5	343	215	813	3.78	21.5	0.360	
4	24.2 $\pm$ 4.2	203 $\pm$ 35	15.8 $\pm$ 5.0	96.4 $\pm$ 30.4	6.32 $\pm$ 1.12	30.3 $\pm$ 5.4	5.38 $\pm$ 1.95	21.3 $\pm$ 7.7	51.7	351	221	832	3.76	22.1	0.368	
8	24.6 $\pm$ 8.8	206 $\pm$ 74	16.4 $\pm$ 5.4	100 $\pm$ 33	6.38 $\pm$ 4.96	30.6 $\pm$ 23.8	5.94 $\pm$ 2.12	23.5 $\pm$ 8.4	53.3	360	232	847	3.65	23.2	0.375	
24	25.2 $\pm$ 8.3	211 $\pm$ 70	17.5 $\pm$ 5.1	107 $\pm$ 31	6.63 $\pm$ 4.15	31.8 $\pm$ 19.9	6.12 $\pm$ 2.11	24.2 $\pm$ 8.4	55.5	374	243	879	3.62	24.3	0.389	
48	25.9 $\pm$ 8.4	217 $\pm$ 71	17.8 $\pm$ 4.0	109 $\pm$ 25	6.78 $\pm$ 3.12	32.5 $\pm$ 14.9	6.44 $\pm$ 3.12	25.5 $\pm$ 12.4	56.9	384	251	902	3.59	25.1	0.399	
96	26.3 $\pm$ 5.2	220 $\pm$ 44	18.4 $\pm$ 5.2	112 $\pm$ 32	7.01 $\pm$ 4.01	33.6 $\pm$ 19.2	6.98 $\pm$ 2.11	27.6 $\pm$ 8.4	58.7	393	262	918	3.50	26.2	0.406	
144	26.8 $\pm$ 4.3	225 $\pm$ 36	18.8 $\pm$ 3.0	115 $\pm$ 18	7.22 $\pm$ 3.13	34.6 $\pm$ 15.0	7.10 $\pm$ 1.95	28.1 $\pm$ 7.7	59.9	403	269	940	3.49	26.9	0.416	

TABLE B-11
 TRIHALOMETHANE CONCENTRATION IN CHLORINATED GROUND WATER AS A FUNCTION OF TIME.
 (pH = 9; Cl₂ = 33.3 x 10⁻⁵ mol/L = 23.6 mg/L; Br⁻ = 1 x 10⁻⁶ mol/L)

Time	Trihalomethanes										Total				Incorporated	
	CHCl ₃		CHCl ₂ Br		CHClBr ₂		CHBr ₃		THM ug/L	THM mol/L x 10 ⁻⁹	THM mol/L x 10 ⁻⁹	Organic		Br	Cl	
	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹				Br mol/L x 10 ⁻⁹	Cl mol/L x 10 ⁻⁹			
Hours																
1	60.9+30.5	510+256	35.3+19.9	215+121	25.9+13.1	124+63	13.1+6.1	51.9+24.1	135	901	619	2080	3.36	61.9	0.625	
2	71.5+18.9	599+158	44.6+18.8	272+115	27.1+10.0	130+48	14.2+8.1	56.2+31.9	157	1060	701	2470	3.52	70.1	0.742	
4	81.9+25.3	686+212	51.5+21.5	314+131	28.5+16.5	137+79	15.3+3.9	60.6+15.6	177	1200	770	2850	3.70	77.0	0.856	
8	95.9+18.9	804+158	62.0+23.5	378+143	31.7+13.7	152+66	18.4+9.5	72.9+37.7	208	1410	901	3320	3.68	90.1	0.997	
24	137+30	1150+248	78.0+44.1	476+269	38.3+15.2	183+73	19.9+3.8	78.8+15.1	273	1890	1080	4590	4.25	108	1.38	
48	195+31	1630+261	95.2+45.2	581+276	46.8+11.5	224+55	21.5+9.5	85.1+37.7	359	2520	1280	6280	4.91	128	1.89	
96	230+35	1930+289	113+38.5	689+235	57.4+18.5	275+89	22.7+3.5	90.0+13.9	423	2980	1510	7440	4.93	151	2.23	
144	255+78	2140+645	133+45.5	811+278	68.8+25.5	330+122	23.1+13.8	91.5+54.7	480	3370	1750	8470	4.84	175	2.54	

TABLE B-12

TRICHALOMETHANE CONCENTRATION IN CHLORINATED GROUND WATER AS A FUNCTION OF TIME.
(pH = 9; $\text{Cl}_2 = 49.9 \times 10^{-5} \text{ mol/L}$; $\text{Br}^- = 1 \times 10^{-6} \text{ mol/L}$)

Time	Trihalomethanes										Total					Incorporated	
	CHCl ₃		CHCl ₂ Br		CHClBr ₂		CHBr ₃		THM	THM	Organic Cl		Br	Cl			
	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	Br mol/L x 10 ⁻⁹	Cl mol/L x 10 ⁻⁹	Cl/Br				
Hours																	
1	89.5±19.5	750±163	50.9±23.5	310±143	30.8±11.5	148±55	16.5±5.6	65.3±22.0	188	1270	802	3020	3.77	80.2	0.605		
2	95.1±15.6	797±131	63.1±30.3	385±185	32.5±6.0	156±29	17.3±4.6	68.5±18.1	208	1410	903	3320	3.68	90.3	0.665		
4	110±28	922±230	70.9±18.9	432±115	36.7±5.6	176±27	18.1±5.1	71.7±20.2	236	1600	999	3810	3.81	99.9	0.764		
8	132±42	1110±345	83.5±25.8	509±157	40.5±12.5	194±60	20.1±5.3	79.6±60.6	276	1890	1140	4540	3.98	114	0.910		
24	195±26	1630±217	100±30	610±184	44.3±16.9	212±81	22.1±13.4	87.5±53.1	361	2540	1300	6320	4.86	130	1.27		
48	244±51	2040±430	106±31	647±186	47.6±5.2	228±30	24.0±6.0	95.0±23.6	422	3010	1390	7640	5.50	139	1.53		
96	290±40	2430±331	116±42	708±254	49.5±2.6	237±12	24.9±3.3	98.6±13.2	480	3470	1480	8940	6.04	148	1.79		
144	314±49	2630±409	126±30	769±180	54.2±3.2	260±15	25.3±4.5	100±18	520	3760	1590	9690	6.09	159	1.94		

Appendix C

TABLE C-1

TRIHALOMETHANE CONCENTRATION IN CHLORINATED GROUND WATER AS A FUNCTION OF TIME.
 (pH = 7; $\text{Cl}_2 = 2.82 \times 10^{-5} \text{ mol/L}$; $\text{Br}^- = 1 \times 10^{-5} \text{ mol/L}$)

Time	Trihalomethanes										Total				Incorporated	
	CHCl ₃		CHCl ₂ Br		CHClBr ₂		CHBr ₃		THM	THM	THM	Organic			Br	Cl
												Br	Cl	Cl/Br		
Hours	ug/L	mol/L $\times 10^{-9}$	ug/L	mol/L $\times 10^{-9}$	ug/L	mol/L $\times 10^{-9}$	ug/L	mol/L $\times 10^{-9}$	ug/L	mol/L $\times 10^{-9}$	mol/L $\times 10^{-9}$	mol/L $\times 10^{-9}$	mol/L $\times 10^{-9}$	mol/L $\times 10^{-9}$	mol/L $\times 10^{-9}$	mol/L $\times 10^{-9}$
1	3.59±0.71	30.1±6.0	3.65±0.52	22.3±3.2	2.81±0.51	13.5±2.4	2.50±1.12	9.90±4.44	12.6	75.8	79.0	148	1.87	0.790	0.525	
2	3.80±1.05	31.8±8.8	3.71±1.15	22.6±7.0	2.88±0.77	13.8±3.7	2.59±0.21	10.3±0.8	13.0	78.5	81.1	154	1.90	0.811	0.546	
4	4.02±0.91	33.7±7.6	3.95±1.09	24.1±6.7	2.95±1.09	14.1±5.2	2.63±1.18	10.4±4.7	13.6	82.3	83.5	163	1.95	0.835	0.578	
8	4.25±0.33	35.6±2.8	4.12±1.03	25.1±6.3	3.14±1.11	15.0±5.3	2.91±2.15	11.5±8.5	14.4	87.2	89.6	172	1.92	0.896	0.610	
24	4.43±1.88	37.1±15.8	4.33±0.95	26.4±5.9	3.19±1.08	15.3±5.2	3.10±2.93	12.3±11.6	15.1	91.1	93.9	179	1.91	0.939	0.635	
48	4.98±1.08	41.7±9.1	4.55±1.17	27.8±7.1	3.22±1.19	15.4±5.7	3.18±1.14	12.6±4.5	15.9	97.5	96.4	196	2.03	0.964	0.695	
96	5.15±1.39	43.2±11.6	4.95±2.18	30.2±13.3	3.25±0.55	15.6±2.6	3.28±1.18	13.0±4.7	16.6	102	100	206	2.06	1.00	0.730	
144	5.21±0.18	43.7±1.5	4.98±1.15	30.4±7.0	3.28±1.05	15.7±5.0	3.49±0.89	13.8±3.5	17.0	104	103	208	2.02	1.03	0.738	

TABLE C-2
 TRIHALOMETHANE CONCENTRATION IN CHLORINATED GROUND WATER AS A FUNCTION OF TIME.
 (pH = 7; Cl₂ = 10.6 x 10⁻⁵ mol/L = 7.50 mg/L; Br⁻ = 1 x 10⁻⁵ mol/L)

Time	Trihalomethanes										Total					Incorporated	
	CHCl ₃		CHCl ₂ Br		CHClBr ₂		CHBr ₃		THM	THM	Organic			Br	Cl		
	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	Br	Cl	Cl/Br				
Hours																	
1	5.22±1.95	43.7±16.3	4.85±2.19	29.6±13.4	2.65±1.15	12.7±5.5	2.51±0.99	9.94±3.92	15.2	95.9	84.8	203	2.39	0.848	0.192		
2	6.45±2.12	45.7±17.8	4.95±2.13	30.2±13.0	2.71±1.05	13.0±5.0	2.59±2.13	10.3±8.4	15.7	99.2	87.1	211	2.42	0.871	0.199		
4	5.95±2.25	49.9±18.9	5.10±1.88	31.1±11.5	2.81±0.88	13.5±4.2	2.69±1.08	10.7±8.4	16.6	105	90.2	225	2.49	0.902	0.212		
8	6.18±3.15	51.8±26.4	5.18±0.98	31.6±6.0	2.93±1.95	14.0±9.3	2.83±1.13	11.2±4.5	17.1	109	93.2	233	2.50	0.932	0.220		
24	6.39±3.41	53.5±28.6	5.33±2.12	32.5±12.9	3.10±1.18	14.8±5.7	2.98±0.75	11.8±3.0	17.8	113	97.5	240	2.46	0.975	0.226		
48	6.89±2.94	57.7±24.6	5.44±3.18	33.2±19.4	3.13±0.95	15.0±4.6	3.05±1.88	12.1±7.4	18.5	118	99.5	255	2.56	0.995	0.241		
96	7.12±5.01	59.7±42.0	5.58±4.01	34.0±24.5	3.19±1.64	15.3±7.9	2.98±2.19	11.8±8.7	18.9	121	100	262	2.62	1.00	0.247		
144	7.93±3.65	66.5±30.6	5.61±2.98	34.2±18.2	3.23±1.09	15.5±5.2	3.20±1.05	12.7±4.2	20.0	129	103	283	2.75	1.03	0.267		

TABLE C-3

TRIHALOMETHANE CONCENTRATION IN CHLORINATED GROUND WATER AS A FUNCTION OF TIME.
(pH = 7; $\text{Cl}_2 = 18.3 \times 10^{-5} \text{ mol/L}$; $\text{Br}^- = 1 \times 10^{-5} \text{ mol/L}$)

Time	Trihalomethanes										Total				Incorporated	
	CHCl ₃		CHCl ₂ Br		CHClBr ₂		CHBr ₃		THM	THM	Organic		Br	Cl		
	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	Br mol/L x 10 ⁻⁹	Cl mol/L x 10 ⁻⁹	Br	Cl		
Hours																
1	30.5±5.8	256±49	18.1±4.8	110±30	6.10±1.95	29.2±9.3	5.01±2.35	19.8±9.3	59.7	415	228	1020	4.47	2.28	0.557	
2	31.3±11.5	262±96	18.3±3.3	112±20	6.21±1.11	29.7±5.3	5.10±2.11	20.2±8.4	60.9	424	232	1040	4.48	2.32	0.568	
4	33.3±10.0	279±83	18.8±6.0	115±36	6.44±1.13	30.8±5.4	5.22±2.29	20.7±9.1	63.8	446	239	1100	4.60	2.39	0.601	
8	35.9±4.8	301±41	19.3±5.1	118±31	6.74±1.81	32.3±8.7	5.41±1.73	21.4±6.9	67.4	473	247	1170	4.74	2.47	0.639	
24	39.5±6.0	331±50	22.1±13.9	135±85	7.11±2.11	34.1±10.1	5.73±2.15	22.7±8.5	74.4	523	271	1300	4.80	2.71	0.710	
48	41.8±8.1	350±68	24.9±8.1	152±50	7.31±1.07	35.0±5.1	5.98±1.98	23.7±7.8	80.0	561	293	1390	4.74	2.93	0.760	
96	44.1±10.8	370±91	26.4±4.8	161±29	7.49±1.84	35.9±8.8	6.10±2.08	24.2±8.2	84.1	591	305	1470	4.82	3.05	0.803	
144	46.8±10.0	392±83	27.7±5.4	169±33	7.99±1.53	38.3±7.3	6.33±2.18	25.1±8.6	88.8	624	321	1550	4.83	3.21	0.847	

TABLE C-4
 TRIHALOMETHANE CONCENTRATION IN CHLORINATED GROUND WATER AS A FUNCTION OF TIME.
 (pH = 7; $\text{Cl}_2 = 22.6 \times 10^{-5} \text{ mol/L} = 16.0 \text{ mg/L}$; $\text{Br}^- = 1 \times 10^{-5} \text{ mol/L}$)

Time Hours	Trihalomethanes										Total				Incorporated	
	CHCl ₃		CHCl ₂ Br		CHClBr ₂		CHBr ₃		THM	THM	Br	Organic		Cl/Br	Br	Cl
	ug/L	mol/L $\times 10^{-9}$	ug/L	mol/L $\times 10^{-9}$	ug/L	mol/L $\times 10^{-9}$	ug/L	mol/L $\times 10^{-9}$	ug/L	mol/L $\times 10^{-9}$		Br	Cl			
1	26.9 $\pm$ 4.2	225 $\pm$ 35	17.3 $\pm$ 4.1	106 $\pm$ 25	5.59 $\pm$ 1.15	26.8 $\pm$ 5.5	5.19 $\pm$ 2.11	20.6 $\pm$ 8.4	55.0	378	220	914		4.15	2.20	0.404
2	29.1 $\pm$ 5.2	244 $\pm$ 43	17.8 $\pm$ 5.2	109 $\pm$ 31	5.95 $\pm$ 3.11	28.5 $\pm$ 14.9	5.22 $\pm$ 1.18	20.7 $\pm$ 4.7	58.1	402	228	979		4.29	2.28	0.433
4	32.1 $\pm$ 8.1	269 $\pm$ 68	18.2 $\pm$ 7.8	111 $\pm$ 47	6.09 $\pm$ 2.16	29.2 $\pm$ 10.4	5.38 $\pm$ 1.94	21.3 $\pm$ 7.7	61.8	431	233	1060		4.55	2.33	0.469
8	33.8 $\pm$ 1.9	283 $\pm$ 16	18.4 $\pm$ 8.1	112 $\pm$ 50	6.20 $\pm$ 1.95	29.7 $\pm$ 9.3	5.44 $\pm$ 3.15	21.5 $\pm$ 12.5	63.8	446	236	1100		4.66	2.36	0.487
24	35.9 $\pm$ 4.3	301 $\pm$ 36	18.9 $\pm$ 6.9	115 $\pm$ 42	6.35 $\pm$ 1.23	30.4 $\pm$ 5.9	5.92 $\pm$ 4.15	23.4 $\pm$ 16.4	67.1	470	246	1160		4.72	2.46	0.513
48	38.5 $\pm$ 4.8	323 $\pm$ 40	20.9 $\pm$ 6.0	127 $\pm$ 36	6.58 $\pm$ 1.92	31.5 $\pm$ 9.2	6.12 $\pm$ 2.15	24.2 $\pm$ 8.5	72.1	506	263	1250		4.75	2.63	0.553
96	39.9 $\pm$ 6.1	334 $\pm$ 51	22.9 $\pm$ 4.9	140 $\pm$ 30	6.90 $\pm$ 1.84	33.1 $\pm$ 8.8	6.21 $\pm$ 1.89	24.6 $\pm$ 7.5	75.9	532	280	1320		4.71	2.80	0.584
144	40.2 $\pm$ 8.3	337 $\pm$ 70	25.1 $\pm$ 4.0	153 $\pm$ 24	6.94 $\pm$ 2.95	33.2 $\pm$ 14.1	6.39 $\pm$ 2.13	25.3 $\pm$ 8.4	78.6	549	295	1350		4.58	2.95	0.597

TABLE C-5
 TRIHALOMETHANE CONCENTRATION IN CHLORINATED GROUND WATER AS A FUNCTION OF TIME.
 (pH = 7; $\text{Cl}_2 = 33.8 \times 10^{-5} \text{ mol/L}$; $\text{Br}^- = 1 \times 10^{-5} \text{ mol/L}$)

Time Hours	Trihalomethanes										Total				Incorporated	
	CHCl ₃		CHCl ₂ Br		CHClBr ₂		CHBr ₃		THM ug/L	THM mol/L $\times 10^{-9}$	THM mol/L $\times 10^{-9}$	Br mol/L $\times 10^{-9}$	Organic Cl		Br	Cl
	ug/L	mol/L $\times 10^{-9}$	ug/L	mol/L $\times 10^{-9}$	ug/L	mol/L $\times 10^{-9}$	ug/L	mol/L $\times 10^{-9}$					Br mol/L $\times 10^{-9}$	Cl mol/L $\times 10^{-9}$		
1	40.1±6.3	336±52	38.5±6.0	235±36	48.9±6.6	234±174	60.3±19.9	239±79	188	1040	1420	1710		1.20	14.2	0.506
2	42.4±8.1	355±68	41.5±8.4	253±51	59.1±9.5	283±46	64.1±20.2	254±80	207	1150	1580	1850		1.17	15.8	0.547
4	44.1±7.2	370±60	48.1±9.9	293±60	69.9±9.0	335±43	79.9±18.8	316±74	242	1310	1910	2030		1.06	19.1	0.601
8	47.1±9.2	395±77	51.3±8.9	313±54	75.1±20.1	360±96	92.5±15.5	366±61	266	1430	2130	2170		1.02	21.3	0.642
24	51.5±10.4	432±87	75.8±5.9	462±36	99.3±14.8	476±71	113±15	447±59	340	1820	2760	2700		0.978	27.6	0.799
48	60.3±11.3	505±95	83.1±8.2	507±50	109±16	522±74	121±23	479±89	373	2010	2470	3050		1.23	24.7	0.902
96	69.9±7.8	586±65	98.1±13.8	598±84	130±26	623±124	145±15	574±59	443	2380	3570	3580		1.00	35.7	1.06
144	75.3±12.2	631±102	101±13	616±76	145±24	695±114	168±25	665±100	489	2610	4000	3820		0.955	40.0	1.13

TABLE C-6
TRIHALOMETHANE CONCENTRATION IN CHLORINATED GROUND WATER AS A FUNCTION OF TIME.
(pH = 7; Cl₂ = 50.8 x 10⁻⁵ mol/L = 36.0 mg/L; Br⁻ = 1 x 10⁻⁵ mol/L.)

Time	Trihalomethanes										Total				Incorporated	
	CHCl ₃		CHCl ₂ Br		CHClBr ₂		CHBr ₃		TUM	TUM	TUM	Organic			Br	Cl
												Br	Cl	Cl/Br		
Hours	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	mol/L x 10 ⁻⁹	mol/L x 10 ⁻⁹	mol/L x 10 ⁻⁹	mol/L x 10 ⁻⁹		
1	48.5±10.2	406±86	51.5±21.7	314±132	65.3±10.5	313±50	80.8±15.9	320±63	246	1350	1900	2160		1.14	19.0	0.425
2	54.3±20.2	455±169	60.3±21.2	368±129	71.3±18.4	342±88	95.3±20.2	377±80	281	1540	2180	2440		1.12	21.8	0.480
4	59.1±10.8	495±91	71.5±15.9	436±97	81.2±5.9	389±28	102±19	404±76	314	1720	2430	2750		1.13	24.3	0.541
8	62.3±13.4	522±112	78.8±18.9	481±115	90.0±10.0	431±48	121±19	479±73	352	1910	2780	2960		1.06	27.8	0.583
24	85.5±9.0	716±75	95.9±22.5	585±137	111±19	532±90	169±29	669±115	461	2500	3660	3850		1.05	36.6	0.758
48	97.5±20.3	817±170	110±35	671±214	138±20	661±96	188±32	744±127	534	2890	4230	4450		1.05	42.3	0.876
96	108±19	905±157	142±23	866±140	166±25	795±117	202±42	800±164	618	3370	4860	5240		1.08	48.6	1.03
144	123±18	1030±150	163±42	994±253	198±21	948±102	241±30	954±119	725	3930	5750	6030		1.05	57.5	1.19

TABLE C-7
TRIHALOMETHANE CONCENTRATION IN CHLORINATED GROUND WATER AS A FUNCTION OF TIME.
($\text{pH} = 9$; $\text{Cl}_2 = 2.82 \times 10^{-5} \text{ mol/L} = 2.00 \text{ mg/L}$; $\text{Br}^- = 1 \times 10^{-5} \text{ mol/L}$)

Time	Trihalomethanes										Total					Incorporated	
	CHCl ₃		CHCl ₂ Br		CHClBr ₂		CBrBr ₃		THM	THM	Organic						
	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹			Br	Cl	Cl/Br				
Hours																	
1	4.01±0.58	33.6±4.9	4.02±1.03	24.5±6.3	3.01±1.13	14.4±5.4	2.83±0.75	11.2±3.0	13.9	83.7	86.9	164	1.89	0.869	0.582		
2	4.09±1.53	34.3±12.8	4.14±0.59	25.3±3.6	3.10±1.08	14.8±5.2	2.98±1.15	11.8±4.6	14.3	86.2	90.3	168	1.86	0.903	0.596		
4	4.25±0.17	35.6±1.4	4.22±0.64	25.7±3.9	3.19±1.13	15.3±5.4	3.15±0.85	12.5±3.4	14.8	89.1	93.8	174	1.86	0.938	0.617		
8	4.44±0.29	37.2±2.4	4.31±2.36	26.3±14.4	3.25±2.15	15.6±10.3	3.20±1.41	12.7±5.6	15.2	91.8	95.6	180	1.88	0.956	0.638		
24	4.95±1.23	41.5±10.3	4.95±1.95	30.2±11.9	3.44±1.14	16.5±5.5	3.25±1.53	12.9±6.1	16.6	101	102	201	1.97	1.02	0.713		
48	5.91±2.02	49.5±16.9	5.01±2.88	31.1±17.6	3.63±3.01	17.4±14.4	3.48±1.18	13.8±4.7	18.1	112	107	228	2.13	1.07	0.809		
96	5.98±1.13	50.1±9.5	5.14±1.95	31.4±11.9	3.77±2.15	18.1±10.3	3.91±0.95	15.5±3.8	18.8	115	114	231	2.03	1.14	0.819		
144	6.20±1.48	52.0±12.4	5.19±2.14	31.7±13.1	3.81±1.95	18.2±9.3	3.99±1.85	15.8±7.3	19.2	118	116	238	2.05	1.16	0.844		

TABLE C-8

TRIHALOMETHANE CONCENTRATION IN CHLORINATED GROUND WATER AS A FUNCTION OF TIME.
 (pH = 9; $\text{Cl}_2 = 10.6 \times 10^{-5} \text{ mol/L} = 7.50 \text{ mg/L}$; $\text{Br}^- = 1 \times 10^{-5} \text{ mol/L}$)

Time Hours	Trihalomethanes										Total				Incorporated	
	CHCl ₃		CHCl ₂ Br		CHClBr ₂		CHBr ₃		THM ug/L	THM mol/L $\times 10^{-9}$	THM mol/L $\times 10^{-9}$	Br mol/L $\times 10^{-9}$	Organic Cl		Br	Cl
	ug/L	mol/L $\times 10^{-9}$	ug/L	mol/L $\times 10^{-9}$	ug/L	mol/L $\times 10^{-9}$	ug/L	mol/L $\times 10^{-9}$					Br mol/L $\times 10^{-9}$	Cl mol/L $\times 10^{-9}$		
1	6.95 $\pm$ 3.01	58.2 $\pm$ 25.2	5.17 $\pm$ 2.05	31.5 $\pm$ 12.5	3.15 $\pm$ 1.11	15.1 $\pm$ 5.3	4.11 $\pm$ 2.08	16.3 $\pm$ 8.2	19.4	121	111	253	2.28	1.11	0.239	
2	7.74 $\pm$ 2.22	64.9 $\pm$ 18.6	5.51 $\pm$ 1.96	33.6 $\pm$ 12.1	3.18 $\pm$ 1.08	15.2 $\pm$ 5.2	4.18 $\pm$ 1.73	16.6 $\pm$ 6.9	20.6	130	114	277	2.43	1.14	0.261	
4	7.94 $\pm$ 1.95	66.5 $\pm$ 16.3	5.84 $\pm$ 2.11	35.6 $\pm$ 12.9	3.21 $\pm$ 1.13	15.4 $\pm$ 5.4	4.29 $\pm$ 1.93	17.0 $\pm$ 7.6	21.3	135	117	286	2.44	1.17	0.270	
8	8.25 $\pm$ 4.02	69.1 $\pm$ 33.7	5.99 $\pm$ 3.16	36.5 $\pm$ 19.3	3.25 $\pm$ 2.11	15.7 $\pm$ 10.1	4.35 $\pm$ 1.08	17.2 $\pm$ 4.3	21.8	139	120	296	2.46	1.20	0.279	
24	8.95 $\pm$ 3.21	75.0 $\pm$ 26.9	6.21 $\pm$ 3.25	37.9 $\pm$ 19.8	3.69 $\pm$ 1.95	17.7 $\pm$ 9.3	4.48 $\pm$ 2.01	17.7 $\pm$ 8.0	23.3	148	126	319	2.53	1.26	0.301	
48	9.05 $\pm$ 2.18	75.8 $\pm$ 18.3	6.34 $\pm$ 4.01	38.7 $\pm$ 24.5	3.78 $\pm$ 1.08	18.1 $\pm$ 5.2	4.95 $\pm$ 2.18	19.6 $\pm$ 8.6	24.1	152	134	323	2.41	1.34	0.305	
96	9.10 $\pm$ 4.10	76.3 $\pm$ 34.4	6.58 $\pm$ 4.11	40.1 $\pm$ 25.1	3.88 $\pm$ 0.85	18.6 $\pm$ 4.1	4.96 $\pm$ 3.01	19.6 $\pm$ 11.9	24.5	155	136	328	2.41	1.36	0.309	
144	9.21 $\pm$ 3.33	77.2 $\pm$ 27.9	6.85 $\pm$ 4.19	41.8 $\pm$ 25.6	4.19 $\pm$ 1.29	20.1 $\pm$ 6.2	4.99 $\pm$ 2.94	19.8 $\pm$ 11.6	25.2	159	141	335	2.38	1.41	0.316	

TABLE C-11
 TRIHALOMETHANE CONCENTRATION IN CHLORINATED GROUND WATER AS A FUNCTION OF TIME.
 (pH = 9; $\text{Cl}_2 = 33.8 \times 10^{-5} \text{ mol/L}$; $\text{Br}^- = 1 \times 10^{-5} \text{ mol/L}$)

Time	Trihalomethanes										Total					Incorporated	
	CHCl ₃		CHCl ₂ Br		CHClBr ₂		CHBr ₃		THM	THM	THM	Organic		Br	Cl		
	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹				Br mol/L x 10 ⁻⁹	Cl mol/L x 10 ⁻⁹				
Hours																	
1	44.5±8.1	373±68	40.5±11.2	247±68	60.9±10.2	292±49	70.8±12.8	280±51	217	1190	1670	1910	1.14	16.7	0.565		
2	49.8±10.8	417±91	44.4±13.4	271±82	69.5±10	333±48	79.5±25.3	315±100	243	1340	1880	2130	1.13	18.8	0.630		
4	54.1±12.5	453±105	49.5±12.5	302±76	73.8±8.3	354±40	84.5±20.2	335±80	262	1440	2020	2320	1.15	20.2	0.686		
8	59.9±10.0	502±84	57.9±10.8	353±66	80.6±9.6	386±46	97.3±23.4	385±93	296	1630	2280	2600	1.14	22.8	0.769		
24	64.5±12.1	541±101	85.8±8.9	523±55	120±15	575±71	137±27	543±108	407	2180	3300	3240	0.982	33.0	0.959		
48	70.9±11.3	594±95	90.5±13.2	552±81	132±20	632±93	149±17	590±67	442	2370	3590	3520	0.981	35.9	1.04		
96	76.6±10.8	642±95	109±16	665±96	152±28	728±136	166±20	657±80	504	2690	4090	3980	0.973	40.9	1.18		
144	88.8±11.9	744±100	119±15	726±89	167±21	800±98	175±29	693±116	550	2960	4410	4480	1.02	44.1	1.33		

TABLE C-12
 TRIHALOMETHANE CONCENTRATION IN CHLORINATED GROUND WATER AS A FUNCTION OF TIME.
 (pH = 9; $\text{Cl}_2 = 50.8 \times 10^{-5} \text{ mol/L}$; $\text{Br}^- = 1 \times 10^{-5} \text{ mol/L}$)

Time	Trihalomethanes								Total						Incorporated	
	CHCl ₃		CHCl ₂ Br		CHClBr ₂		CHBr ₃		THM	THM	Organic					
	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹			Br mol/L x 10 ⁻⁹	Cl mol/L x 10 ⁻⁹	Cl/Br	Br	Cl	
Hours																
1	55.1±22.2	462±186	61.5±9.9	375±60	75.1±20.1	360±96	101±20	400±79	293	1600	2300	2500	1.09	23.0	0.492	
2	59.2±20.1	496±168	68.3±13.8	417±84	82.1±23.1	393±111	131±22	519±85	341	1890	2760	2720	0.986	27.6	0.535	
4	65.5±18.9	549±158	76.9±20.1	469±123	91.5±24.1	438±115	168±19	665±75	402	2120	3340	3020	0.904	33.4	0.594	
8	71.2±7.4	597±62	80.0±19.9	488±121	98.3±22.1	471±106	188±25	744±100	438	2300	3660	3240	0.885	36.6	0.638	
24	90.3±18.8	757±158	108±16	659±96	129±30	618±144	218±32	863±127	545	2900	4480	4210	0.940	44.8	0.829	
48	110±9	922±78	132±23	805±137	151±30	723±143	245±43	970±170	638	3420	5160	5100	0.988	51.6	1.00	
96	130±19	1090±158	165±30	1010±184	198±39	948±187	298±38	1180±150	791	4230	6450	6240	0.967	64.5	1.23	
144	148±30	1240±247	181±30	1100±181	216±42	1030±199	348±50	1380±198	893	4750	7300	6950	0.952	73.0	1.37	

TABLE D-2

TRIHALOMETHANE CONCENTRATION IN CHLORINATED GROUND WATER AS A FUNCTION OF TIME.
(pH = 7; $\text{Cl}_2 = 11.3 \times 10^{-5} \text{ mol/L} = 8.00 \text{ mg/L}$; $\text{Br}^- = 1 \times 10^{-4} \text{ mol/L}$)

Time	Trihalomethanes										Total				Incorporated	
	CHCl ₃		CHCl ₂ Br		CHClBr ₂		CHBr ₃		THM	THM	Organic			Br	Cl	
	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	mol/L x 10 ⁻⁹	Br	Cl	Cl/Br		
Hours																
1	4.07±1.12	34.1±9.4	5.01±2.32	30.6±14.2	8.15±1.15	39.0±5.5	12.1±5.3	47.9±21.1	29.3	152	252	203	0.806	0.252	0.180	
2	4.19±1.29	35.1±10.8	5.23±1.34	31.9±8.2	8.53±0.75	40.9±3.6	12.4±5.0	49.1±19.8	30.4	157	261	210	0.805	0.261	0.186	
4	4.27±0.19	35.8±1.6	5.68±1.95	34.6±11.9	8.95±1.25	42.9±6.0	13.1±1.8	51.9±7.1	32.0	165	276	220	0.797	0.276	0.195	
8	4.39±0.08	36.8±0.7	5.98±3.11	36.5±19.0	9.50±0.59	45.5±2.8	14.1±2.0	55.8±7.7	34.0	175	295	229	0.776	0.295	0.203	
24	5.29±1.12	44.3±9.4	7.01±0.21	42.8±1.3	10.5±2.2	50.3±10.3	16.9±3.2	66.9±12.6	40.0	204	344	269	0.782	0.344	0.238	
48	5.52±0.14	46.3±1.2	7.15±3.29	43.6±20.1	10.7±1.2	51.3±5.7	17.3±7.3	68.5±28.9	40.7	210	352	277	0.787	0.352	0.245	
96	5.69±1.95	47.7±16.3	7.45±0.28	45.4±1.7	10.9±2.0	52.2±9.8	17.9±4.1	70.9±16.3	42.0	216	363	287	0.791	0.363	0.254	
144	5.98±2.15	50.1±18.0	7.69±1.23	46.9±7.5	11.1±3.3	53.2±15.9	18.3±6.0	72.5±23.7	43.1	223	371	297	0.801	0.371	0.263	

TABLE D-3
TRIHALOMETHANE CONCENTRATION IN CHLORINATED GROUND WATER AS A FUNCTION OF TIME.
(pH = 7; Cl₂ = 16.9 x 10⁻⁵ mol/L = 12.0 mg/L; Br⁻ = 1 x 10⁻⁴ mol/L)

Time	Trihalomethanes										Total				Incorporated	
	CHCl ₃		CHCl ₂ Br		CHClBr ₂		CHBr ₃		THM ug/L	THM mol/L x 10 ⁻⁹	THM mol/L x 10 ⁻⁹	Br	Organic		Br	Cl
	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹					Cl	Cl/Br		
1	5.21±2.13	43.7±17.8	9.55±1.75	58.3±10.7	22.3±5.8	107±30	39.5±6.5	156±26	76.6	365	740	355	0.480	0.740	0.210	
2	5.35±0.75	44.8±6.3	9.86±0.75	60.1±4.6	24.4±7.1	117±34	43.5±2.2	172±9	83.1	394	810	372	0.459	0.810	0.220	
4	5.80±1.82	48.6±15.3	10.2±2.3	62.2±14.3	29.5±11.9	141±57	47.2±13.1	187±52	92.7	439	905	411	0.454	0.905	0.243	
8	6.10±0.55	51.1±4.6	10.8±1.2	65.9±7.3	33.2±12.5	159±60	51.1±3.8	202±15	101	478	990	444	0.448	0.990	0.263	
24	7.10±2.12	59.5±17.8	11.8±2.2	72.0±13.1	43.5±13.4	208±64	62.3±3.3	247±13	125	587	1230	531	0.432	1.23	0.314	
48	7.45±1.13	62.4±9.5	12.2±1.2	74.4±7.2	48.6±4.6	233±22	66.6±1.8	264±7	135	634	1330	569	0.428	1.33	0.337	
96	7.88±1.83	66.0±15.3	12.9±1.8	78.7±11.2	55.5±7.2	266±34	75.3±12.1	298±48	152	709	1500	621	0.414	1.50	0.367	
144	8.01±1.45	67.1±12.2	13.2±1.0	80.5±5.8	58.3±3.4	279±15	77.1±11.1	305±44	157	732	1550	641	0.414	1.55	0.380	

TABLE D-4
 TRIHALOMETHANE CONCENTRATION IN CHLORINATED GROUND WATER AS A FUNCTION OF TIME.
 (pH = 7; Cl₂ = 22.6 x 10⁻⁵ mol/L; Br⁻ = 1 x 10⁻⁴ mol/L)

Time	Trihalomethanes										Total				Incorporated	
	CHCl ₃		CHCl ₂ Br		CHClBr ₂		CHBr ₃		THM	THM mol/L x 10 ⁻⁹	Organic				Br	Cl
											Br	Cl	Cl/Br	Cl/Br		
Hours	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	mol/L x 10 ⁻⁹	mol/L x 10 ⁻⁹	mol/L x 10 ⁻⁹	mol/L x 10 ⁻⁹		
1	4.01±2.32	33.6±19.4	6.20±3.31	37.8±20.2	15.8±1.9	75.7±5.7	20.1±5.3	79.6±21.0	46.1	227	428	252	0.589	0.428	0.112	
2	4.11±1.19	34.4±10.0	6.25±1.81	38.1±11.0	16.1±3.0	77.1±14.1	22.2±3.4	87.9±13.4	48.7	238	456	257	0.564	0.456	0.114	
4	4.15±1.22	34.8±10.2	6.44±0.91	39.3±5.6	16.8±9.3	80.5±44.6	24.4±4.6	96.6±18.1	51.8	251	490	264	0.539	0.490	0.117	
8	4.20±0.15	35.2±1.3	6.71±1.51	40.9±9.2	17.4±9.2	83.3±44.2	28.9±3.2	114±13	57.2	273	550	271	0.493	0.550	0.120	
24	5.10±3.14	42.7±26.3	7.83±2.05	47.8±12.5	22.0±3.1	105±15	36.5±14.1	145±56	71.4	341	693	327	0.472	0.693	0.145	
48	5.15±1.15	43.2±9.6	7.98±1.81	48.1±11.0	25.3±10.1	121±48	39.5±12.1	156±48	77.9	368	758	347	0.458	0.758	0.154	
96	5.20±1.10	43.6±9.2	8.13±2.15	49.6±13.1	29.4±9.9	141±48	41.9±5.1	166±20	84.6	400	830	371	0.447	0.830	0.164	
144	5.22±2.30	43.7±19.3	8.20±0.33	50.0±2.0	32.2±5.8	154±28	44.0±11.9	174±47	89.6	422	880	385	0.438	0.880	0.170	

TABLE D-5

TRIHALOMETHANE CONCENTRATION IN CHLORINATED GROUND WATER AS A FUNCTION OF TIME.
(pH = 7; $\text{Cl}_2 = 32.4 \times 10^{-5} \text{ mol/L} = 23.0 \text{ mg/L}$; $\text{Br}^- = 1 \times 10^{-4} \text{ mol/L}$)

Time	Trihalomethanes										Total					Incorporated	
	CHCl ₃		CHCl ₂ Br		CHClBr ₂		CHBr ₃		THM ug/L	THM mol/L x 10 ⁻⁹	THM mol/L x 10 ⁻⁹	Organic			Br	Cl	
	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹				Br mol/L x 10 ⁻⁹	Cl mol/L x 10 ⁻⁹	Cl/Br			
Hours																	
1	6.30±1.15	52.8±9.6	21.5±5.4	131±33	49.5±3.0	237±14	80.1±13.0	317±52	157	738	1560	657	0.421	1.56	0.203		
2	6.71±1.19	56.2±10.0	25.9±3.8	158±23	54.8±3.9	262±19	84.5±6.0	335±24	171	811	1690	747	0.442	1.69	0.231		
4	7.01±2.34	58.7±19.6	31.5±7.9	192±48	59.9±11.2	287±54	99.5±5.4	394±21	198	932	1950	847	0.434	1.95	0.261		
8	7.46±1.93	62.5±16.2	36.8±2.0	224±12	65.9±14.5	316±70	113±32	447±125	223	1050	2200	952	0.433	2.20	0.294		
24	8.52±2.14	71.4±17.9	47.1±3.4	287±21	78.1±3.6	374±17	141±15	558±59	275	1290	2710	1160	0.428	2.71	0.358		
48	8.88±1.10	74.4±9.2	51.2±9.6	312±58	84.5±13.1	405±63	168±28	665±111	313	1460	3120	1250	0.401	3.12	0.386		
96	9.23±0.59	77.3±4.9	53.8±5.0	328±30	98.8±11.3	473±54	193±44	764±174	355	1640	3570	1360	0.381	3.57	0.420		
144	9.68±1.32	81.1±11.0	55.5±1.1	339±7	103±5	493±24	203±6	804±24	371	1720	3740	1410	0.377	3.74	0.435		

TABLE D-6

TRIHALOMETHANE CONCENTRATION IN CHLORINATED GROUND WATER AS A FUNCTION OF TIME.
($\text{pH} = 7$; $\text{Cl}_2 = 49.4 \times 10^{-5} \text{ mol/L}$; $\text{Br}^- = 35.0 \text{ mg/L}$; $\text{Br}^- = 1 \times 10^{-4} \text{ mol/L}$)

Time	Trihalomethanes										Total				Incorporated	
	CHCl ₃		CHCl ₂ Br		CHClBr ₂		CHBr ₃		THM	THM	THM	Br	Cl	Organic	Br	Cl
	ug/L	mol/L $\times 10^{-9}$	ug/L	mol/L $\times 10^{-9}$	ug/L	mol/L $\times 10^{-9}$	ug/L	mol/L $\times 10^{-9}$	ug/L	ug/L	mol/L $\times 10^{-9}$	mol/L $\times 10^{-9}$	mol/L $\times 10^{-9}$	mol/L $\times 10^{-9}$	mol/L $\times 10^{-9}$	mol/L $\times 10^{-9}$
1	7.86 $\pm$ 2.11	65.9 $\pm$ 17.7	40.1 $\pm$ 18.5	245 $\pm$ 113	62.5 $\pm$ 29.0	299 $\pm$ 140	198 $\pm$ 40	784 $\pm$ 156	308	1390	3200	987	0.308		3.20	0.200
2	7.93 $\pm$ 1.15	66.5 $\pm$ 9.6	44.5 $\pm$ 9.0	271 $\pm$ 55	68.8 $\pm$ 5.0	330 $\pm$ 24	259 $\pm$ 15	1030 $\pm$ 57	380	1700	4020	1070	0.266		4.02	0.217
4	8.15 $\pm$ 4.41	68.3 $\pm$ 37.0	48.5 $\pm$ 5.3	296 $\pm$ 32	74.8 $\pm$ 19.5	358 $\pm$ 93	309 $\pm$ 50	1220 $\pm$ 196	440	1940	4670	1150	0.246		4.67	0.233
8	8.43 $\pm$ 2.51	70.6 $\pm$ 21.0	53.8 $\pm$ 12.5	328 $\pm$ 76	80.1 $\pm$ 25.3	384 $\pm$ 121	466 $\pm$ 68	1850 $\pm$ 271	608	2630	6650	1250	0.188		6.65	0.253
24	9.51 $\pm$ 3.19	79.7 $\pm$ 26.7	65.0 $\pm$ 13.3	397 $\pm$ 81	92.2 $\pm$ 18.8	442 $\pm$ 90	554 $\pm$ 54	2190 $\pm$ 215	721	3100	7850	1480	0.189		7.85	0.300
48	10.6 $\pm$ 8.3	88.8 $\pm$ 69.6	72.3 $\pm$ 19.1	441 $\pm$ 117	109 $\pm$ 18	522 $\pm$ 86	613 $\pm$ 23	2430 $\pm$ 89	805	3480	8780	1670	0.190		8.78	0.338
96	11.2 $\pm$ 3.4	93.9 $\pm$ 28.0	79.5 $\pm$ 25.1	485 $\pm$ 153	131 $\pm$ 25	627 $\pm$ 122	817 $\pm$ 85	3240 $\pm$ 335	1040	4450	11500	1880	0.163		11.5	0.381
144	11.8 $\pm$ 8.9	98.9 $\pm$ 74.4	88.9 $\pm$ 11.5	542 $\pm$ 70	151 $\pm$ 10	723 $\pm$ 47	985 $\pm$ 120	3900 $\pm$ 475	1240	5260	13700	2100	0.153		13.7	0.425

TABLE D-8
 TRIHALOMETHANE CONCENTRATION IN CHLORINATED GROUND WATER AS A FUNCTION OF TIME.
 (pH = 9; $\text{Cl}_2 = 11.3 \times 10^{-5} \text{ mol/L} = 8.00 \text{ mg/L}$; $\text{Br}^- = 1 \times 10^{-4} \text{ mol/L}$)

Time	Trihalomethanes										Total				Incorporated	
	CHCl ₃		CHCl ₂ Br		CHClBr ₂		CHBr ₃		THM	THM	THM	Organic			Br	Cl
Hours	ug/L	mol/L $\times 10^{-9}$	ug/L	mol/L $\times 10^{-9}$	ug/L	mol/L $\times 10^{-9}$	ug/L	mol/L $\times 10^{-9}$	ug/L	mol/L $\times 10^{-9}$	ug/L	Br	Cl	Cl/Br	Br	Cl
1	5.95 $\pm$ 0.21	49.6 $\pm$ 1.8	6.25 $\pm$ 0.12	38.1 $\pm$ 0.7	10.7 $\pm$ 3.6	51.3 $\pm$ 17.2	16.1 $\pm$ 3.6	63.8 $\pm$ 14.1	39.0	203	332	276	0.831	0.332	0.244	
2	6.12 $\pm$ 1.02	51.3 $\pm$ 8.6	6.32 $\pm$ 2.31	38.6 $\pm$ 14.1	11.8 $\pm$ 0.2	56.5 $\pm$ 0.9	16.5 $\pm$ 4.9	65.3 $\pm$ 19.2	40.7	212	348	288	0.828	0.348	0.255	
4	6.16 $\pm$ 1.13	51.6 $\pm$ 9.5	6.88 $\pm$ 1.78	42.0 $\pm$ 10.9	12.5 $\pm$ 1.2	59.9 $\pm$ 5.5	17.1 $\pm$ 5.2	67.7 $\pm$ 20.6	42.6	221	365	299	0.819	0.365	0.265	
8	6.29 $\pm$ 0.18	52.7 $\pm$ 1.5	7.18 $\pm$ 0.55	43.8 $\pm$ 3.4	12.7 $\pm$ 2.5	60.8 $\pm$ 11.7	18.3 $\pm$ 3.2	72.5 $\pm$ 12.7	44.5	230	383	307	0.802	0.383	0.272	
24	7.18 $\pm$ 0.88	60.2 $\pm$ 7.4	8.11 $\pm$ 1.91	49.5 $\pm$ 11.7	13.9 $\pm$ 3.3	66.7 $\pm$ 16.0	23.2 $\pm$ 4.5	91.9 $\pm$ 17.6	52.4	268	459	346	0.754	0.459	0.306	
48	7.25 $\pm$ 2.18	60.8 $\pm$ 18.3	8.35 $\pm$ 2.22	50.9 $\pm$ 13.5	14.2 $\pm$ 5.3	68.0 $\pm$ 25.5	24.5 $\pm$ 2.0	97.0 $\pm$ 7.7	54.3	277	478	352	0.736	0.478	0.312	
96	7.41 $\pm$ 2.01	62.1 $\pm$ 16.8	8.55 $\pm$ 3.19	52.2 $\pm$ 19.5	18.1 $\pm$ 3.3	77.1 $\pm$ 15.8	26.1 $\pm$ 6.0	103 $\pm$ 24	58.2	294	515	368	0.715	0.515	0.326	
144	7.68 $\pm$ 2.15	64.4 $\pm$ 18.0	8.79 $\pm$ 3.31	53.6 $\pm$ 20.2	17.2 $\pm$ 2.0	82.4 $\pm$ 9.3	27.9 $\pm$ 7.0	110 $\pm$ 28	61.6	310	548	383	0.699	0.548	0.339	

TABLE D-9

TRIHALOMETHANE CONCENTRATION IN CHLORINATED GROUND WATER AS A FUNCTION OF TIME.
 (pH = 9; $\text{Cl}_2 = 16.9 \times 10^{-5} \text{ mol/L}$; $\text{Br}^- = 12.0 \text{ mg/L}$; $\text{Br}^- = 1 \times 10^{-4} \text{ mol/L}$)

Time	Trihalomethanes										Total				Incorporated	
	CHCl ₃		CHCl ₂ Br		CHClBr ₂		CHBr ₃		THM	THM	THM	Br	Organic		Br	Cl
Hours	ug/L	mol/L $\times 10^{-9}$	ug/L	mol/L $\times 10^{-9}$	ug/L	mol/L $\times 10^{-9}$	ug/L	mol/L $\times 10^{-9}$	ug/L	mol/L $\times 10^{-9}$	ug/L	mol/L $\times 10^{-9}$	Br	Cl	Br	Cl
1	6.32 $\pm$ 2.30	53.0 $\pm$ 19.3	14.5 $\pm$ 3.2	88.5 $\pm$ 19.6	36.0 $\pm$ 13.1	172 $\pm$ 63	63.3 $\pm$ 3.2	251 $\pm$ 13	120	565	1190	508		0.427	1.19	0.301
2	6.44 $\pm$ 0.92	54.0 $\pm$ 7.7	15.2 $\pm$ 2.0	92.7 $\pm$ 12.1	38.4 $\pm$ 7.3	184 $\pm$ 35	68.1 $\pm$ 14.2	270 $\pm$ 56	128	601	1270	531		0.418	1.27	0.314
4	6.75 $\pm$ 1.12	56.6 $\pm$ 9.4	15.7 $\pm$ 1.6	95.8 $\pm$ 9.6	43.4 $\pm$ 2.0	208 $\pm$ 9	71.5 $\pm$ 4.6	283 $\pm$ 18	137	643	1360	569		0.418	1.36	0.337
8	6.99 $\pm$ 1.14	58.6 $\pm$ 9.6	16.1 $\pm$ 2.2	98.2 $\pm$ 13.5	46.6 $\pm$ 6.6	223 $\pm$ 32	77.1 $\pm$ 15.1	305 $\pm$ 60	147	685	1460	595		0.408	1.46	0.352
24	7.88 $\pm$ 2.13	66.0 $\pm$ 17.8	17.3 $\pm$ 2.2	106 $\pm$ 14	58.1 $\pm$ 5.9	278 $\pm$ 29	88.8 $\pm$ 11.4	352 $\pm$ 45	172	802	1720	688		0.400	1.72	0.407
48	7.99 $\pm$ 1.13	67.0 $\pm$ 9.5	17.9 $\pm$ 1.1	109 $\pm$ 7	61.9 $\pm$ 9.8	297 $\pm$ 47	92.1 $\pm$ 10.3	365 $\pm$ 41	180	848	1800	716		0.398	1.80	0.424
96	8.13 $\pm$ 0.14	68.1 $\pm$ 1.2	18.3 $\pm$ 3.4	112 $\pm$ 21	66.6 $\pm$ 7.3	319 $\pm$ 35	94.5 $\pm$ 9.6	374 $\pm$ 38	188	873	1870	747		0.399	1.87	0.442
144	8.33 $\pm$ 1.12	69.8 $\pm$ 9.4	18.8 $\pm$ 3.1	115 $\pm$ 19	70.9 $\pm$ 9.0	340 $\pm$ 43	95.3 $\pm$ 14.5	377 $\pm$ 57	193	902	1930	779		0.404	1.93	0.461

TABLE D-10
 TRIHALOMETHANE CONCENTRATION IN CHLORINATED GROUND WATER AS A FUNCTION OF TIME.
 (pH = 9; $\text{Cl}_2 = 22.6 \times 10^{-5} \text{ mol/L}$; $\text{Br}^- = 1 \times 10^{-4} \text{ mol/L}$)

Time Hours	Trihalomethanes										Total				Incorporated	
	CHCl_3 ug/L		CHCl_2Br ug/L		CHClBr_2 ug/L		CHBr_3 ug/L		THM mol/L $\times 10^{-9}$	THM ug/L	THM mol/L $\times 10^{-9}$	Organic			Br	Cl
												Br	Cl	Cl/Br		
1	4.98 $\pm$ 0.23	41.7 $\pm$ 1.9	9.30 $\pm$ 0.2	56.7 $\pm$ 1.2	22.1 $\pm$ 3.8	106 $\pm$ 18	34.1 $\pm$ 8.9	135 $\pm$ 35	339	70.5	339	674	345	0.512	0.674	0.153
2	5.00 $\pm$ 1.12	41.9 $\pm$ 9.4	9.55 $\pm$ 3.12	58.3 $\pm$ 19.0	22.9 $\pm$ 6.0	110 $\pm$ 29	36.7 $\pm$ 2.2	145 $\pm$ 9	355	74.2	355	713	352	0.494	0.713	0.156
4	5.20 $\pm$ 2.15	43.6 $\pm$ 18.0	10.1 $\pm$ 2.2	61.6 $\pm$ 13.4	24.8 $\pm$ 3.8	119 $\pm$ 18	40.5 $\pm$ 1.2	160 $\pm$ 5	384	80.6	384	780	373	0.478	0.780	0.165
8	5.44 $\pm$ 3.17	45.6 $\pm$ 26.6	10.4 $\pm$ 1.1	63.4 $\pm$ 6.6	28.7 $\pm$ 10.1	137 $\pm$ 48	43.8 $\pm$ 5.2	173 $\pm$ 21	419	88.3	419	856	401	0.468	0.856	0.177
24	6.10 $\pm$ 3.23	51.1 $\pm$ 27.0	11.4 $\pm$ 2.8	69.5 $\pm$ 17.1	34.9 $\pm$ 3.6	167 $\pm$ 17	52.9 $\pm$ 10.2	209 $\pm$ 40	497	105	497	1030	459	0.446	1.03	0.203
48	6.18 $\pm$ 5.51	51.8 $\pm$ 46.2	11.9 $\pm$ 3.1	72.6 $\pm$ 18.8	39.5 $\pm$ 4.1	189 $\pm$ 20	58.4 $\pm$ 9.6	231 $\pm$ 40	544	116	544	1140	490	0.430	1.14	0.217
96	6.24 $\pm$ 6.31	52.3 $\pm$ 52.9	12.5 $\pm$ 1.2	76.3 $\pm$ 7.0	42.9 $\pm$ 1.2	205 $\pm$ 6	62.3 $\pm$ 11.9	247 $\pm$ 47	581	124	581	1230	515	0.419	1.23	0.228
144	6.31 $\pm$ 1.35	52.9 $\pm$ 11.3	12.9 $\pm$ 4.8	78.7 $\pm$ 29.0	45.3 $\pm$ 11.2	208 $\pm$ 54	65.0 $\pm$ 5.0	257 $\pm$ 20	597	130	597	1270	524	0.413	1.27	0.232

TABLE D-11
 TRIHALOMETHANE CONCENTRATION IN CHLORINATED GROUND WATER AS A FUNCTION OF TIME.
 (pH = 9; $\text{Cl}_2 = 32.4 \times 10^{-5} \text{ mol/L} = 23.0 \text{ mg/L}$; $\text{Br}^- = 1 \times 10^{-4} \text{ mol/L}$)

Time	Trihalomethanes										Total					Incorporated	
	CHCl ₃		CHCl ₂ Br		CHClBr ₂		CHBr ₃		THM	THM	THM	Organic				Br	Cl
	ug/L	mol/L $\times 10^{-9}$	ug/L	mol/L $\times 10^{-9}$	ug/L	mol/L $\times 10^{-9}$	ug/L	mol/L $\times 10^{-9}$	ug/L	ug/L	ug/L	Br	Cl	Cl/Br	Cl/Br		
1	7.78 $\pm$ 2.15	65.2 $\pm$ 18.0	30.9 $\pm$ 11.3	188 $\pm$ 69	68.5 $\pm$ 13.2	328 $\pm$ 63	198 $\pm$ 11	784 $\pm$ 43	305	1370	3200	899	0.281			3.20	0.277
2	8.23 $\pm$ 1.05	70.0 $\pm$ 8.8	33.5 $\pm$ 10.8	204 $\pm$ 66	75.6 $\pm$ 8.0	362 $\pm$ 38	231 $\pm$ 25	915 $\pm$ 100	348	1550	3700	980	0.265			3.70	0.302
4	8.44 $\pm$ 0.53	70.7 $\pm$ 4.4	36.4 $\pm$ 4.8	222 $\pm$ 29	80.1 $\pm$ 4.0	384 $\pm$ 19	293 $\pm$ 15	1160 $\pm$ 59	418	1840	4500	1040	0.231			4.50	0.321
8	8.99 $\pm$ 1.14	75.3 $\pm$ 9.6	40.5 $\pm$ 5.4	247 $\pm$ 33	90.3 $\pm$ 5.0	433 $\pm$ 24	369 $\pm$ 35	1460 $\pm$ 137	509	2220	5500	1150	0.209			5.50	0.355
24	9.98 $\pm$ 3.33	83.6 $\pm$ 27.9	51.5 $\pm$ 5.3	314 $\pm$ 32	113 $\pm$ 22	541 $\pm$ 105	444 $\pm$ 59	1760 $\pm$ 234	618	2700	6680	1420	0.213			6.68	0.438
48	10.5 $\pm$ 2.3	88.0 $\pm$ 19.6	59.8 $\pm$ 7.9	365 $\pm$ 48	125 $\pm$ 32	599 $\pm$ 155	522 $\pm$ 40	2070 $\pm$ 158	717	3120	7780	1590	0.204			7.78	0.491
96	11.3 $\pm$ 1.6	94.7 $\pm$ 13.0	68.2 $\pm$ 4.3	416 $\pm$ 295	145 $\pm$ 13	695 $\pm$ 60	645 $\pm$ 69	2550 $\pm$ 271	870	3760	9460	1810	0.191			9.46	0.559
144	11.8 $\pm$ 4.3	98.9 $\pm$ 36.4	72.2 $\pm$ 8.1	440 $\pm$ 50	164 $\pm$ 16	786 $\pm$ 76	678 $\pm$ 26	2680 $\pm$ 103	926	4000	10100	1960	0.194			10.1	0.605

TABLE D-12

TRIHALOMETHANE CONCENTRATION IN CHLORINATED GROUND WATER AS A FUNCTION OF TIME.
 (pH = 9; Cl₂ = 49.4 x 10⁻⁵ mol/L = 35.0 mg/L; Br⁻ = 1 x 10⁻⁴ mol/L)

Time	Trihalomethanes										Total				Incorporated	
	CHCl ₃		CHCl ₂ Br		CHClBr ₂		CHBr ₃		THM	THM	Organic		Cl/Br		Br	Cl
											Br	Cl				
Hours	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	ug/L	mol/L x 10 ⁻⁹	mol/L x 10 ⁻⁹	mol/L x 10 ⁻⁹				
1	9.10±3.75	76.3±31.4	59.5±4.4	363±27	83.5±32.0	400±153	266±53	1050±210	418	1890	4310	1350	0.313		4.31	0.273
2	9.35±2.25	78.4±18.9	64.4±3.2	393±20	89.9±23.0	431±110	313±24	1240±94	477	2140	4980	1450	0.291		4.98	0.294
4	9.80±0.19	82.1±1.6	69.9±11.8	426±72	96.6±18.8	463±90	358±20	1420±79	534	2390	5610	1560	0.278		5.61	0.316
8	10.3±5.1	86.3±42.8	76.6±9.4	467±58	111±24	532±115	448±39	1770±154	646	2850	6840	1720	0.251		6.84	0.348
24	11.5±4.0	96.4±33.1	87.8±5.6	536±34	131±32	627±153	605±66	2400±261	835	3660	8990	1990	0.221		8.99	0.403
48	12.0±8.1	101±68	95.2±11.5	581±70	150±9	719±43	725±100	2870±395	982	4270	10600	2180	0.206		10.6	0.441
96	12.8±9.9	107±83	118±33	720±201	188±19	901±91	1010±103	4000±408	1330	5730	14500	2660	0.183		14.5	0.538
144	13.4±5.3	112±45	131±11	799±64	195±13	934±62	1130±151	4470±598	1470	6320	16100	2870	0.178		16.1	0.581